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(Communicated at the meeting of April 27, 1929).

Dans quelques communications antérieures ¹) un de nous (en collaboration avec ses élèves) a montré que les acides perbenzoïques et peracétiques agissent d'une manière individuelle sur la liaison double.

L'acide perbenzoïque ou réactif de Prelishajew donne presque toujours l'éthylène-oxyde correspondant, tandis que l'acide peracétique forme souvent l'acétate de l'α-glycol.

Mais soit qu'on hydrolyse l'oxyde ou qu'on obtient directement le glycol le résultat définitif est toujours le même: pendent la formation du glycol une réversion moléculaire de Walden s'est accomplie.

Les cyclohexènes et cyclopentènes p. ex. donnent exclusivement les *trans-diols.* Seulement quand un groupe aromatique est lié à un des atomes de carbone insaturés le trans-diol est mélangé avec une quantité plus ou moins considérable de son isomère cis.

Le permanganate en solution alcaline donnant toujours le "cis-glycol", mais souvent avec des rendements médiocres nous avons dans la combinaison des deux méthodes d'oxidation le moyen pour décéler la configuration des polyalcools et aussi des alcylènes dont nous sommes partis.

Le butène obtenu par deshydration du méthyl-éthyl carbinol p. ex. donne principalement le diméthyl 2,3 glycol asymmétrique, il est par conséquence le cis-butène.

Un de nous (W. C. Smit) a appliqué la méthode aux peracides sur quelques acides insaturés aliphatiques avec 18 atomes de carbone.

Après avoir préparé le mélange d'acides linoliques 9.12, qu'on obtient par débromuration du tétrabromure p. d. f. 115° ²) et les avoir transformés en éthers méthyliques.

Ceux-ci sont oxidés d'abord avec l'acide perbenzoïque.

Nous avons isolé un seul éther méthylique d'un acide dioxidostéarique avec un rendement de 40⁰/₀ p. d. f. = 31°. En considérant que notre point de départ est un mélange d'acides linoliques et que nous pouvons

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¹) Recueil des trav. chim. des P. B. **45**. 838, 914 (1926) **47**. 683, 694, 839 (1928) et **48**. 363 (1929).

²) Avec l'exception de l'acide tétrabromostéarique p. d. f. 74°5 obtenu par M. v. d. Steur, Diss. Delft 1928 par bromuration de l'acide linolélaidique 9—12, l'acide p. d. f. 114° est le seul acide de ce genre connu avec certitude. Tous les autres acides mentionnés dans la littérature avec des pts de fusion plus bas sont probablement les éthers éthyliques ou méthyliques.

obtenir au moins quatre acides dioxidostéariques stéréoisomères — cis-cis', trans-trans', cis'-trans et cis-trans' — ce rendement n'est pas mal.

Cet éther méthylique donne en le saponifiant à basse température un acide dioxidostéarique p. d. f. 79°.

Pour hydrolyser l'anneau triatomique de l'éthylène oxyde nous l'avons traité par de l'acide sulfurique dilué à 80° et par de l'acide sulfurique de 80°/₀ à 0°.

La première méthode nous donna un acide tétrahydroxystéarique p. d. f. 95°, la deuxième méthode un isomère fondant à 148°.

Ces deux acides sont donc différents des *acides sativiques* obtenus par oxidation de l'acide linolique par du permanganate de potassium.

Il y a cependant peu de certitude sur ces acides; Rollet [1]) n'obtient qu'un seul acide fondant à 171—173°, tandis que Nicolet et Cox [2]) mentionnent „two different sativic acids m.p. 170° et 153° respectively". Ils disent qu'ils ont obtenu par moyen de l'acide hypochlorique ou hypobromique deux autres acides fondant à 144° et 135°; il est donc possible que l'acide 148° soit identique avec l'acide 144° de Nicolet et Cox. Quant à nos acides il faut remarquer que nous ne savons rien d'absolu de leurs configurations, seulement le *rapport* en est connu; ils sont formés tous les deux du même acide par hydrolyse de deux anneaux triatomiques en solution acide (sans groupes aromatiques); il y a donc réversion moléculaire.

L'acide peracétique nous donna le même résultat; l'éther méthylique de l'acide linolique nous fournit un éther d'un acide dioxidostéarique fondant à 31°, en le saponifiant nous obtenions l'acide au p. d. f. 79°.

Oxidation de l'acide *linolique 9.11.* Cet acide a été préparé pour la première fois par Mangold [3]), par distillation a pression réduite de l'acide ricinélaidique, mais la composition n'en était pas encore connu.

M. W. C. SMIT a préparé cet acide de la même manière et en a déterminé la réfraction moléculaire à 77° = 88.9 calculé selon Eisenlohr = 85.9. Cet exaltation de quatre unités montre que nous avons affaire avec un système conjugué. Le nombre de iode (Wijs) = 130 (calculé = 181.1) beaucoup trop bas confirmait la présence de ce système.

La composition en était déterminée définitivement par ozonisation; nous avons obtenu de 25 gr. de l'acide 13 gr. de l'acide azélaique p.d.f. 106° et 14 gr. du sel de zinc d'un acide monobasique.

L'acide lui-même passa à 220° (pr. 76 cm.); le poids moléculaire fut 130.6 et l'analyse donna $C = 64.6\,\%$, $H = 10.5$.

Les constantes pour l'acide heptanoique sont:

P. d. éb. ($P = 76$ cm.) = 223, Pds. $Mol = 130.1$, $C = 64.6$ et $H = 10.8$.

L'amide était identique avec l'amide de l'aide heptanoique synthétique.

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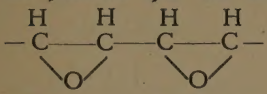
[1]) Z. physiol. Ch. **62**, 420 (1909).

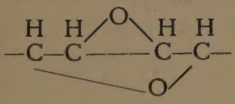
[2]) J. Am. Chem. Soc. **44**, 144 (1922).

[3]) Sitz. Berl. Akad. Wiss., 1894, pag. 277.

Outre ces deux produits principaux de la décomposition il a obtenu 0.323 gr. d'acide carbonique, très peu d'une substance volatile ayant les propriétés d'acétaldehyde et un sirop réducteur très soluble dans de l'eau, dont nous n'avons pas pu isoler un dérivé connu. Il n'est cependant pas douteux que l'acide linolique de Mangold est *l'ac. octodécadiénique 9.11.*

L'éther méthylique de cet acide oxidé par de l'acide perbenzoïque en solution chloroformique donna un éther méthylique d'un acide dioxidostéarique fondant à 47°.

Par saponification deux acides dioxidostéariques à p.d.f. 89° et 75° y furent isolés M. Smit n'a pas réussi à hydrolyser ces deux acides; il est possible que ces acides avec les anneaux triatomiques voisins:  offrent une résistance stérique envers cette opération, mais il n'est pas exclus qu'ils aient une autre composition, peut-être:



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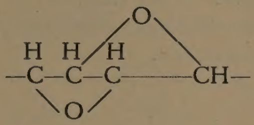
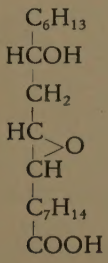


L'oxidation de l'éther méthylique de l'ac. ricinélaidique donna des résultats intéressants mais prévus par la théorie.

Avec l'acide perbenzoïque en solution chloroformique il donna l'éther de l'acide oxidoricinélaidique, probablement un mélange de deux substances, car en saponifiant à basse température *deux* acides oxidoélaidiques furent obtenus fondant à 64° et 59° et ayant des rotations spécifiques différentes et opposées, viz. $[\alpha]_D^{17^\circ} = -17^\circ.2$ et $+3^\circ.4$ que nous pouvons donner les symboles arbitraires en acceptant que l'acide ricinélaidique soit l'acide trans



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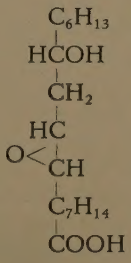
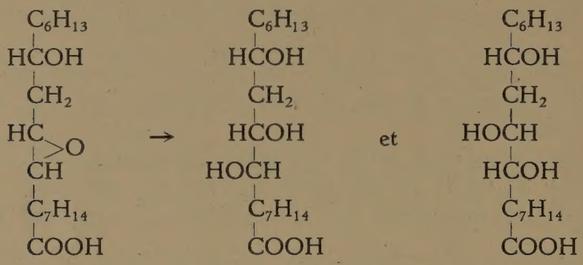


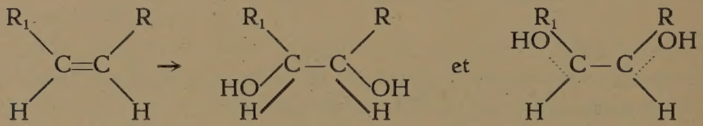
Souvent l'oxidation était suivie par une hydrolyse, alors se forment aussi *deux* acides trihydroxystéarique fondant à 137° et 112°.

Nous pouvons accepter que pendant cette formation il se manifeste une transposition de Walden, les deux groupes hydroxyles se placent donc opposés l'un envers l'autre:



qui ne sont pas des stéréomères optiquement opposés, parceque le groupe $C_6H_{13}CHOHCH_2$ contient un centre asymmétrique constant, dextrogyre.

Je veux observer que les acides obtenus par HAZURA et GRÜSNER [1]) en oxidant l'acide ricinoléique avec du permanganate de potassium (c. à d. sans réversion de Walden) sont probablent identiques avec les acides décrits ci-dessus.



L'acide peracétique étant assez stable nous en avons profité pour voir s'il est possible, par la détermination de la vitesse de l'oxidation, à distinguer les acides oléiques et élaidiques, resp. les acides ricinoléiques et ricinélaidiques; en effet la vitesse des deux acides naturels est beaucoup plus grande que celle de leurs isomères. $K^{18°}_{\text{ac. ol.}} = 0.036$; $K^{18°}_{\text{ac. él.}} = 0.023$; $K^{18°}_{\text{ac. ric. ol.}} = 0.026$; $K^{18°}_{\text{ac. ric. él.}} = 0.016$.

Plus nous avons examinés si les acides plus insaturés à système conjugué se distinguent des acides à système insaturé isolé.

Le système conjugué est plus rapidement oxydé au début que le système isolé, mais après quelque temps ce rapport est renversé. Il est curieux que les substances à système conjugué exigent plus d'acide peracétique que calculé; il paraît que l'oxidation ne s'arrête avec l'addition de deux (trois) molécules. Par ces différences nous avons une nouvelle méthode pour caractériser les systèmes conjugués et c'est de cette manière que nous pouvions montrer que dans les acides α- et β-éléostéariques se trouve un système de trois liaisons insaturées conjuguées.

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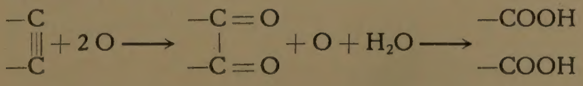
[1]) J. Ch. Soc. 54. Abth., 1270 (1888); ils donnent les p. d. f. 110—111° et 141°—142°.

Dans la plupart des huiles et des graisses naturelles les doubles liaisons sont isolées et on pouvait attendre qu'on pouvait employer l'acide peracétique pour déterminer le degré d'insaturation; or nous l'avons comparé avec la méthode iodométrique de Wijs; les chiffres ci-dessous donnent un aperçu qui montre clairement que cette supposition était exacte.

Substance	Nombre d'iode		Nombre peracétique Calc. comme n. d'iode	
	Calc.	Wijs	Après 20 h.	Après 2 × 24 h.
Ac. oléique	89.9	89.7	90.6	91.0
Ac. linolique 9.12	181.1	179.0	177.7	180.6
Ether éthylique de l'acide linoléique 9, 12, 15	248.6	248.0	231.5	246.5
Huile d'olive		82.7	83.0	82.3
„ de safflower		138.6	137.7	139.2
„ de lin		179.9	180.0	179.7
„ de graines de soya		111.9	112.0	112.5
„ de ricin		83.7	84.8	84.9
„ de navette		100.6	100.0	101.5

Le réactif pouvant être obtenu très aisément et étant assez stable on peut employer cette méthode à côté de celle de Wijs.

L'oxidation de la liaison acétylénique par l'ac. peracétique (avec M. Slooff). Nous avons examiné d'abord l'acétylène lui-même en le faisant barboter par une solution acétique de l'ac. peracétique de 10 $^0/_0$ et en agitant énergiquement; il n'avait lieu aucune action. Puis nous avons choisi l'acide stéarolique; celui-ci est attaqué mais beaucoup plus lentement que les substances à liaisons doubles, p. ex. nul dégagement de chaleur ne pouvait être observé. En revanche la liaison triple exige beaucoup plus qu'une molécule de l'oxydant. Probablement la réaction principale est la formation d'un acide dicétonique, qui est ensuite sciendé en deux tronçons acides.



$$\begin{array}{l}-C\\ \;\;|||\\ -C\end{array} + 2\,O \longrightarrow \begin{array}{l}-C=O\\ \;\;|\\ -C=O\end{array} + O + H_2O \longrightarrow \begin{array}{l}-COOH\\ \\ -COOH\end{array}$$

Mais il se forme aussi un acide monocétonique, peut-être par hydratation simple, comme avec de l'acide sulfurique concentré. Nous avons oxydé ensuite les acides undéciniques 9 et 10; tandis que le premier avec le groupe $CH_3C\equiv C$ — est attaqué environ avec la même vitesse que l'acide stéarolique, le dernier avec le groupe $HC\equiv C$ — est oxydé si lentement que la réaction n'est pas terminée après quelques semaines. Il paraît donc que l'atome hydrogène caractéristique exerce une action protectrice envers l'acide peracétique.

Action des hydrocarbures saturés sur le benzoylperoxyde (avec M. Gaster) M. Gelissen [1]) seul et en collaboration avec M. Hermans [2]) puis M. Reynhart [3]) ont trouvé qu'une grande diversité de substances organiques agissent sur le dibenzoylperoxyde sans catalyseurs et à une temp. de 60 à 100° d'une manière analogue. Ces réactions peuvent être schématisées généralement par deux équations:

$$[C_6H_5COO]_2 + RH \begin{cases} \longrightarrow CO_2 + C_6H_5COO\underline{R} + C_6H_5\underline{H} \\ \longrightarrow CO_2 + C_6H_5COO\underline{H} + C_6H_5\underline{R} \end{cases}$$

Aussi quelques chlorures organiques subissent la même transformation. Il se montrait cependant que non seulement les substances avec des atomes d'hydrogène ou de chlore mobiles sont attaquées, mais M. Reynhart avait trouvé que même le tétrachloroéthylène est décomposé d'une manière tout-à-fait analogue et M. Gelissen a montré que le cyclohexane qui ressemble à presque tous les égards aux paraffines donne du phénylcyclohexane et de l'ac. benzoïque.

Il paraît donc que même l'hydrogène des paraffines peut entrer en réaction avec la molécule très active des peroxydes.

Pour vérifier cette déduction nous avons faire bouillir une fraction d'éther de pétrole (exempt d'aromates) passant entre 100° et 102° avec le peroxyde.

La décomposition a lieu très régulièrement et il se dégage une molecule d'acide carbonique.

Les autres produits obtenus de la manière decrite dans la littérature étaient de l'acide benzoïque (± 60 $^0/_0$), un éther heptylique de l'acide benzoïque, un homologue du benzène et des produits de l'action ultérieure des produits primaires sur le peroxyde.

Le cours de la réaction principale est donc certainent celui du schème donné ci-dessus.

L'éther benzoïque, donnait par saponification *un alcool tertiaire*, ce que signifie que parmi les hydrocarbures du mélange complexe des paraffines surtout un heptane à atome de carbone tertiaire fut attaqué. Nous avons donc trouvé une synthèse directe d'un alcool tertiaire en

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1) Thèse de doctorat à sc. techniques. Delft 1925.

2) Berichte D. chem. Gesellsch. **50** 285, 476, 480, 764, 984, 2396 (1925).

3) These de doct. à sc. techn. Delft (1926) et Recueil trav. chim. P.B. 46,59—76 (1927).

partant de paraffines et montré que l'action du peroxyde a un caractère sélectif.

Pour vérifier cette déduction nous avons préparé l'octane normal, qui ne contient pas un atome d'hydrogène tertiaire. En effet cet hydrocarbure fut attaqué beaucoup plus lentement, quoique la temperature de la réaction fût plus élevée (124° au lieu de 100°).

Le cours de la réaction est d'ailleurs le même qu'avec l'éther de pétrole, mais la quantité des produits secondaires était beaucoup plus grande.

Delft, Mars 1929.

Chemistry. — *Cataphoretic measurements and the theory of the critical potential.* By H. R. KRUYT and D. R. BRIGGS[1].

(Communicated at the meeting of April 27, 1929).

Stability of a lyophobic colloid system, which is the inverse function of the rate at which flocculation takes place, is governed by the electric charge on the surface of the colloid particle. HARDY (Z. physik. Chem. **33**, 385 (1900)) considered that flocculation would not take place until the potential had been lowered to zero, i.e., that even the smallest charge on the particle was sufficient to render it stable. POWIS (Z. physik. Chem. **89**, 186, (1915)) working with oil droplets in water found, however, that flocculation occurred when the cataphoretic velocity had yet a value considerably higher than zero and that flocculation was brought about by that concentration of electrolyte which was just sufficient to reduce the cataphoretic velocity to this value, the potential corresponding to which he named "the critical potential". He was able to repeat these results with the As_2S_3 sol (J. Chem. Soc. **109**, 734 (1916)) with the exception that, in this case, salts of monovalent cations brought about precepitation at a concentration of the salt for which the cataphoretic velocity was found to be still very much higher than that velocity which was "critical" for the polyvalent cation salts and indeed almost as high as that exhibited by the original sol. FREUNDLICH & ZEH (Z. f. physik. Chem. **114**, 65 (1925)), KRUYT, ROODVOETS & VAN DER WILLIGEN (Colloid Symp. **4**, 304 (1926)), KRUYT and VAN DER WILLIGEN (Z. physik. Chem. **130**, 170 (1927)) and MUKHERJEE (Nature, **122**, 960 (1928)) among others, have had the same experience, that is, the salts of the alkali metals (and of hydrogen) cause precipitation of the colloids at concentrations for which the cataphoretic velocity of the particles is sometimes as high as or even higher than of the original sol.

However, it has been assumed that the potential across the double layer is always proportional to the cataphoretic velocity. The at present accepted equation designating this relationship is a modification of the Lamb-Helmholtz equation and is

$$\zeta = \frac{6\pi\eta}{D} u$$

where $\zeta =$ electrocinetic potential
$u =$ cataphoretic velocity
$\eta =$ viscosity of medium
$D =$ dielectric constant.

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[1] National Research Council (U. S. A.) Fellow.

Following work by FÜRTH (Physik. Zeitschr. **25**, 676 (1924)) and PECHHOLD (Ann. d. Physik. **83**, 427 (1927)) on the variation of the dielectric constant of solutions of electrolytes, in which it was shown that the dielectric constant shows first a small decrease followed by a sharp increase as the concentration of electrolyte is increased, KRUYT and VAN DER WILLIGEN (Z. Physik. Chem. **130**, 170 (1927)) ascribed the exceptional behavior of these alkali cation salts to their influence on this factor in the high concentrations needed to bring about flocculation. It is evident from the above equation that if D were increased in value with increase in concentration of the salt, the cataphoretic velocity (u) could remain constant or even increase while ζ at the same time decreased. If, then, the ζ potential on the particle is counted the stabilising influence, its being lowered to the critical value could still be postulated even though the migration velocity remained high, by a corresponding increase in the dielectric constant. It is to be pointed out that this large increase in D is required to occur only in the interfacial region and that the corresponding value for the bulk of the solution does not need to change to a corresponding degree. Adsorption on the surface of the sol particle could account for a marked increase in concentration of electrolyte in that region needed to account for the larger change in D in that vicinity.

It seems, then, that the exceptional behavior of the monovalent cation salts is due to the fact that relatively high concentrations of these salts are necessary to bring about flocculation and that, at these higher concentrations there is introduced a secondary effect which causes anomalous values to be ascribed to the electrocinetic potential at the flocculation concentrations. The object of the present investigation was to find if POWIS' theory holds when only small concentrations of those monovalent cations which are very highly adsorbed and which bring about flocculation in concentrations of comparable molality to those required for polyvalent cation salts. Such salts are those of strychnine and new fuchsin.

Experimental.

The method used for measuring the cataphoretic velocity of the sols was a modified *U*-tube method developed by KRUYT and VAN DER WILLIGEN (Koll. Zeitschr. **44**, 22, (1928)) in which a four electrode cell is employed, the two inner electrodes being placed at a known distance apart in the two arms of the *U*-tube and kept at a definite difference of potential throughout the experiment. The liquid used above the sol in all cases was the ultrafiltrate of the sol with or without the electrolyte as the case might be. The electrolyte was added to the sol before ultrafiltration so that the ultrafiltrate might be truly that of the sample of sol being worked with. Ultrafiltration was accomplished in a manner adapted from the method of Bechold-Intlohn (Z. f. angew. Chem. **37**, 494 (1924)) and adequately described in the paper by KRUYT and VAN DER WILLIGEN.

A thin collodion membrane supported by a porous porcelain cup acted as the filter and allowed a fairly rapid filtration to be accomplished.

VAN DER WILLIGEN found that the rate of migration of the rising interface between the sol and its ultrafiltrate was proportional to the fall in potential per unit length in the column of ultrafiltrate, while the falling interface advanced at a rate proportional to the fall in potential per unit length in the column of sol, that is, each interface, for a given potential drop between the inner electrodes, advanced at a rate which was directly proportional to the specific resistance of the medium into which it advanced. He gave, as the average velocity (u) of migration

$$u = \frac{w_1 h_1 + w_2 h_2}{ZE}$$

where w_1 and w_2 are the observed distances moved by the rising and falling interfaces, respectively ; h_1 and h_2, the average length of ultrafiltrate and of sol, respectively, lying between the inner electrodes across which is maintained the constant potential drop E during the time Z of the observation.

This relation seems to hold very well with a sol in which no settling effect is observable after it has been run into the U-tube. Such is the case with the As_2S_3-sol but not with the other sols used in these experiments. What this settling is due to is not exactly known but it seems to be a contraction of the sol which continues at an ever decreasing rate for some time after the sol is slowly let into the U-tube under the clear overlying solution (u-filtrate). If the sol is placed into the U-tube with no clear liquid above it, no settling occurs. The effect seems most noticable when the number of particles is least. With the gold sol and the selenium sol, both of which show it, the difference between the specific conductivity of the sol and of its ultrafiltrate was found to be so small (Table I), that no difference would have been noticed between the migration rates of the two interfaces had not the settling effect been present. Since the settling occurred at the same rate in each arm of the U-tube, it was necessary only to take the average, distance moved as ½ the sum in the calculation of u

$$u = \frac{\frac{1}{2}(w_1 + w_2) H}{ZE}$$

where H represents the length between the two inner electrodes across which the potential difference E is kept constant for time Z and w_1 and w_2 are the distances moved by the rising and falling interfaces respectively, during the time Z.

The flocculation values used in this research were those obtained when 2 cc. of electrolyte solution was added unformly from a pipette to 10 cc. of the sol contained in a precipitation tube, the resulting solution uniformly mixed by rotational shaking before setting aside to be again shaken 24 hours later and finally observed after another ½ hour. The flocculation value was taken as that concentration of electrolyte which, through the above process, just gave a perfectly clear liquid above the coagulum. The selenium sol was very slow to settle after disturbance so that the flocculation values observed with it were those after 24 hours without further shaking. With the gold sol it is of interest to note that this flocculation value does not coincide with the change in colour from red to blue but requires a higher concentration of electrolyte.

In preparing the sol for the cataphoretic measurements the stock sol was always increased in volume by 20 %, the added liquid being pure water in cases where measurements on the pure sol were to be carried out, or an electrolyte solution of sufficient concentration to give the resulting sol the required concentration for the experiment. The electrolyte solution was always added to the sol in a manner as nearly as possible the same as that when adding it to determine the flocculation value. In both cases the percentage increase in volume due to added liquid was the same.

When the flocculation value had been obtained for a salt, the cataphoretic velocity was found for from 4 to 6 concentrations of this electrolyte, these concentrations usually being equally spaced between zero concentration and 90 % of the flocculation concentration. In this manner the trend of the curve could be found and extrapolation to the flocculation concentration made with a fair degree of accuracy. Cataphoretic measurements were carried out at 20° C. ± 1° C., in a water bath. The usual potential difference maintained between the two inner electrodes was 18 Volts ; this was lower in cases where the electrolyte content was high enough to allow sufficient current to pass to cause heating of the liquid in the *U*-tube, in which cases as low as 10 Volts was the potential maintained.

The As_2S_3 sol was prepared in the common way (See e.g. KRUYT and v. D. SPEK (Koll. Z. **25**, 1, (1919)). 3 Grams of As_2O_3 were dissolved in 500 cc. distilled water at the boiling temperature, this solution being then added, drop by drop, to 200 cc. of distilled water which was kept saturated with washed H_2S gas the entire time during which the As_2O_3 solution was being added. When the reaction was complete the excess H_2S gas was removed by bubbling through the sol hydrogen gas which had previously been washed consecutively through alkaline $KMnO_4$, $HgCl_2$, NaOH solutions and water. The sol was kept until a short time before use at the concentration at which it was prepared but was diluted with four volumes of distilled water before the measurements were carried out with it. The diluted sol thus contained approximatily 1.06 grams of As_2S_3 per liter.

The selenium sol was prepared according to directions modified from those given by KRUYT and VAN ARKEL (Koll. Z., **32**, 29 (1923)) by bringing to the boiling temperature 550 cc. of doubly distilled water to which had been added 30 cc. of a 1.2 molar solution of hydrazine hydrate, then adding quickly 25 cc. of a 0.1 molar solution of SeO_2, and finally after the sol had reached a salmon yellow colour, 5 cc. more of the same solution were added. The containing flask was then removed from the flame. To this solution should be added 2½ liters of water but experiment showed this resulting sol to contain too much electrolyte for our purpose. To free the sol from this electrolyte it was found possible to ultrafilter the sol prepared as above until nearly all electrolyte was removed (as its specific conductivity, Table I, clearly shows) and then adding water until the sol reached about the density of colour that it would have shown had the water been added before the electrolyte was removed. This purification by ultrafiltration, which is essentially a rapid dialysis is not successful with all sols but so long as the selenium sol was not freed entirely from liquid it could be again successfully dispersed by shaking in a fresh volume of water. This sol contained approximately 0.05 gram of selenium per liter. The particles of selenium sol were fairly large when viewed in the ultramicroscope but the sol was stable.

For some reason, probably because of the relatively large size of the particles, this washed selenium sol was found very difficult with which to obtain consistent results and the values are more erratic than are those obtained with the other sols.

The red gold sol was that of TEMMINCK GROLL (Chem. Weekblad **13**, 617 (1916)) prepared by using H_2O_2 as the reducing agent. 330 cc. of the sol was prepared at a time, it being found impossible to prepare larger volumes successfully. To make 330 cc. of sol, 25 cc. of 3 % H_2O_2 were added to 250 cc. of doubly distilled water and to this was added, a drop at a time with constant and vigorous shaking, 30 cc. of a 0.066 % $NaAuCl_4$ solution, followed by 2 cc. of 0.1 N NaOH, then 20 cc. of the 0.066 % $NaAuCl_4$ solution and finally 3 cc. of 0.1 N NaOH. Each quantity thusly prepared was allowed to stand, with occasional shaking, for 30 minutes before it was added to the stock sol. Under the ultramicroscope this sol showed the characteristic green particles of a red gold sol. It contained 0.06 grams of gold per liter and was about 0.0015 normal in alkali which was probably present as Na_2CO_3 and $NaHCO_3$. It did not cause phenolphtalein to turn pink.

TABLE I.

Specific conductivities of the sols, diluted with the $^1/_5$ vol. of distilled water, and of their ultrafiltrates.

Sol	$\varkappa$ (for sol) $\times 10^6$	$\varkappa$ (for U-filtrate) $\times 10^6$	Ratio $\frac{\varkappa_{uF}}{\varkappa_{sol}}$
As_2S_3	37.50	16.20	0.451
Se	3.31	3.14	0.949
Au	188.00	185.00	0.984

TABLE II.

The flocculation values and the initial and critical cataphoretic velocities of the various sols with the electrolytes used.

	As_2S_3 sol		Se sol		Au sol	
	Flocculation value millimols per liter	Cataph. veloc. μ/volt. sec.	Floc. value m. mol per liter	Cataph. veloc. μ/volt. sec.	Floc. value m. mol per liter	Cataph. veloc. μ/volt. sec.
Initial value	—	4.6	—	3.4	—	3.9
Strychnine NO_3	0.098	1.7	0.018	2.3	0.41	2.15
New fuchsin Cl	0.117	1.7	—	—	—	—
$BaCl_2$	0.60	1.65	2.85	2.0	0.47	2.15
$AlCl_3$	0.042	1.55	0.0018	2.0	0.0043	2.1
KCl	60.0	3.4	16.6	2.2	24.0	3.65

Results and discussion.

The accompanying graphs show very clearly in every case that the monovalent cations which are highly adsorbed and cause flocculation at low concentrations, reduce the cataphoretic migration velocity uniformly to approximately the same value at the concentration of total precipitation as that which is characteristic of the polyvalent ions at their corresponding concentrations. Table II gives the flocculation concentrations for these salts and the approximate extrapolated value for the migration velocity at these concentrations together with the migration velocity for the original sol.

There are several things about these curves which are not entirely clear. It is difficult at present to explain why $BaCl_2$ should uniformly give a curve in which the cataphoretic velocity is reduced very quickly to a value very near to that shown at the concentration of complete precipitation, after which the curve is nearly flat for more than half its length on the concentration axis. There is indication that the flocculation value decreases with time. For example, with the Se sol the flocculation value after the sol had stood with the salt in it for 6 days was found to have changed to the neighbourhood of 1.35 millimols per liter instead of 2.85 millimols per liter as indicated at the end of 24 hours. This form of curve is general for $BaCl_2$ and may repay a closer examination. There is no reason to expect that it should differ markedly from that shown by $AlCl_3$ or the highly adsorbed monovalent cation salt. Another unexpected result was that shown by $AlCl_3$ with the gold sol. There is a probable explanation for this however, and that lies in the fact that there was a very small concentration of alkali present in the gold sol. This alkali promptly reacted with the $AlCl_3$ to form $Al(OH)_3$ and thus removed the Al^{+++} ion from the solution. The $Al(OH)_3$ particles were probably carrying only a very slight positive charge because of the presence of the remaining alkali in the sol. Not until most of this alkali was removed by the added $AlCl_3$ was it possible for the Al^{+++} ions to remain in the solution and therefore

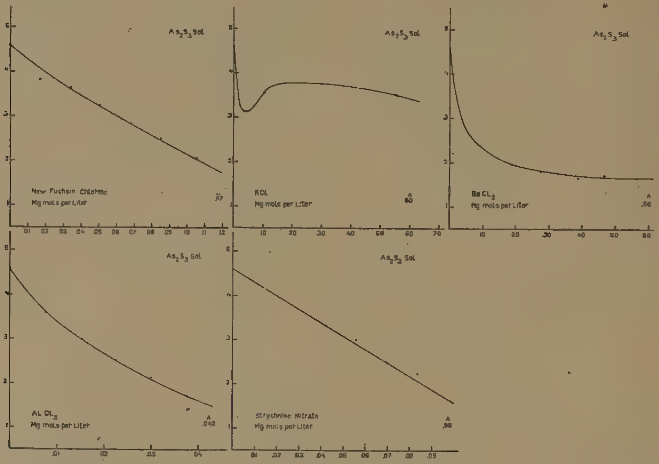
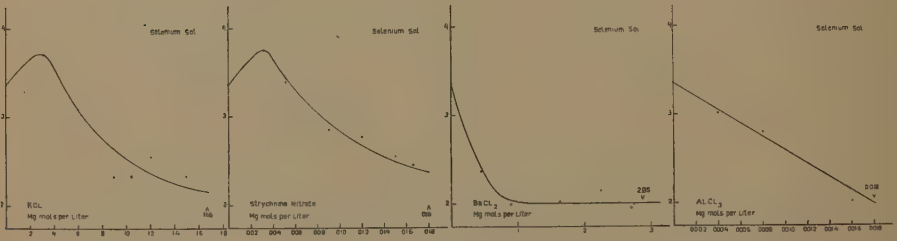


Fig. 1.



Fig, 2.

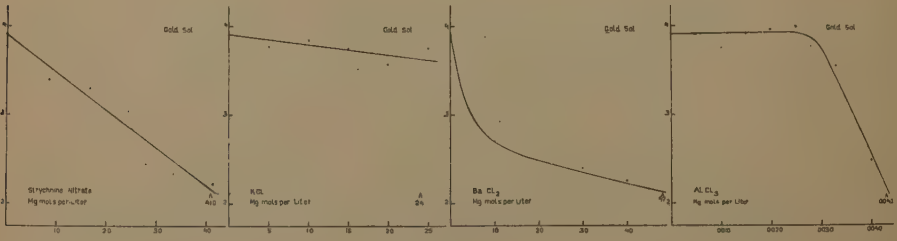


Fig. 3.

be adsorbed by the gold sol to reduce its ζ potential, whereupon only a very small amount of Al^{+++} ions sufficed to precipitate the sol. It is interesting that so long as no reduction of the cataphoretic velocity (up to 0.0025 millimols $AlCl_3$ per liter) was found, the gold sol retained its original red colour but at 0.0028 millimols per liter the sol had already turned blue though total precipitation after 24 hours occurred at a much higher concentration (0.0043 millimols per liter). In the case of the Se-sol, too, where the electrolyte content of the sol itself was very low, it is interesting that KCl reduced the cataphoretic velocity to a value near that of the other electrolytes at the flocculation concentration.

There are, indeed, a good many more unanswered question arising from these results than there are those which have found an answer. However, the real object of the research, namely to find if the POWIS' rule holds for monovalent cation electrolytes when these can cause precipitation at concentrations of the same order as those required for polyvalent cation salts, has been successfully answered in the affirmative without a doubt. We can safely say that when flocculation can be brought about in low concentrations of electrolytes the migration velocity is always reduced to the same value when precipitation occurs.

One of us (D. R. B.) will publish presently an extended paper in which more data will be given and in which details will be fully discussed.

April 1929.

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Chemistry. — *The osmotic vapour-pressure,* II. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of April 27, 1929).

In the osmotic equilibrium:

$$(L)\,P \mid M(W) \mid (W\ vapour)\,\pi_w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is a liquid L under the pressure P on the left side of the membrane $M(W)$ and on the right side W-vapour under the pressure π_w. If we increase the pressure on the right side of membrane a little, then some W-vapour will condense right through the membrane into the liquid; if we decrease the pressure a little, then some water will evaporate from the liquid through the membrane. Consequently π_w is the pressure with which the liquid L presses the W-vapour through the membrane; for this reason we have called π_w the *O.W.V.P.* (Osmotic-Water-Vapour-Pressure) of the liquid L.

Besides the W-vapour of (1) we now also bring the vapours of the other substances A, B, C etc.; then we get an osmotic equilibrium, which we shall represent by:

$$(L)\,P \mid M(W) \mid \left(\begin{matrix} aA + bB \ldots + wW \\ vapour \end{matrix}\right)\pi \quad . \quad . \quad . \quad (2)$$

So on the right side of the membrane is a mixture of vapours of the composition:

$$a\ mol\ A + b\ mol\ B, \ldots + w\ mol\ W \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which:

$$a + b \ldots + w = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The added substances A, B etc. may be components of the liquid L; they may also represent strange substances, however, viz. substances, not occurring in the liquid L. We assume that the gas-laws obtain for this mixture of vapours.

We imagine the mixture of vapours (3) in a space under a pressure π; if only the W-vapour were present in this space, the pressure in this space would not be π, but smaller, viz. $w\pi$; this pressure $w\pi$ is the partial $V.P.$ of the W-vapour in the mixture of vapours.

In system (1) the pressure of the W-vapour on the membrane is π_w; as the substances A, B etc. of the mixture of vapours in (2) have no influence on the diffusion of the W-vapour through the membrane, the pressure of the W-vapour in this mixture of vapours must, therefore, also be π_w. So we may say:

when a liquid is in osmotic equilibrium with a mixture of vapours by means of a membrane, the partial *V.P.* of the *W*-vapour of this mixture of vapours will be equal to π_w, viz. equal to the *O.W.V.P.* of the liquid.

Hence follows that between π and π_w the ratio:

$$w\pi = \pi_w \quad \text{or} \quad \pi = \frac{\pi_w}{w} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

exists.

We now compare the osmotic equilibria (1) and (2) viz.

$$(L)\, P \mid M(W) \mid (W\ vapour)\, \pi_w \quad . \quad . \quad . \quad . \quad . \quad (6^a)$$

$$(L)\, P \mid M(W) \mid \left(\begin{matrix} aA + bB \ldots + wW \\ vapour \end{matrix} \right) \pi \qquad \pi = \frac{\pi_w}{w} \quad . \quad (6^b)$$

which both have a membrane $M(W)$. Here π_w is the *O.W.V.P.* of the liquid; consequently π_w has a determined value, only depending on the composition and the pressure of the liquid L.

The pressure π of the mixture of vapours can have an infinite number of values, however; for, as is shown by (6^b), it depends not only upon π_w, but also upon w, viz. upon the *W*-amount of the mixture of vapours. It appears from (6^b) that π is always greater than π_w, but that it approaches π_w more closely as w increases; when w becomes $= 1$, so that the vapour in (6^b) only consists of *W*-vapour and (6^b) consequently passes into (6^a), π becomes $= \pi_w$; so we may consider (6^a) also as a special case of (6^b).

It appears from the preceding that in general we may say:

when a liquid is in osmotic equilibrium with a mixture of vapours by means of a membrane $M(W)$, the pressure π of this mixture will be equal to $\pi_w : w$ viz. the *O.W.V.P.* of the liquid, divided by the *W*-amount of the vapour.

When S is also a volatile substance of the liquid L, then we can with the aid of a membrane $M(S)$ get the osmotic equilibria:

$$L(P) \mid M(S) \mid (S\text{-}vapour)\, \pi_s \quad . \quad . \quad . \quad . \quad . \quad . \quad (7^a)$$

$$L(P) \mid M(S) \mid \left(\begin{matrix} aA + bB \ldots + sS \\ vapour \end{matrix} \right) \pi \qquad \pi = \frac{\pi_s}{s} \quad . \quad . \quad (7^b)$$

Consequently π_s here is the *O.S.V.P.* of the liquid. We now find $\pi = \pi_s : s$. So from this follows for any substance S:

when a liquid is in osmotic equilibrium with a mixture of vapours by means of a membrane $M(S)$, the pressure π of this mixture is equal to $\pi_s : s$ viz. the *O.S.V.P.* of the liquid, divided by the *S*-amount of the vapour.

We now take a liquid L, containing the volatile substances X, Y, Z, W etc. With the aid of the membranes indicated we then can obtain the osmotic equilibria:

$$(L)\,P \mid M(X) \mid (X\text{-}vapour)\,\pi_x \quad \ldots\ldots\ldots \quad (8^a)$$

$$(L)\,P \mid M(Y) \mid (Y\text{-}vapour)\,\pi_y \quad \ldots\ldots\ldots \quad (8^b)$$

$$(L)\,P \mid M(Z) \mid (Z\text{-}vapour)\,\pi_z \quad \ldots\ldots\ldots \quad (8^c)$$

$$(L)\,P \mid M(W) \mid (W\text{-}vapour)\,\pi_w \quad \ldots\ldots\ldots \quad (8^d)$$

etc. With the aid of a membrane $M(n)$ we then get an osmotic equilibrium:

$$(L)\,P \mid M(n) \mid \left(\begin{matrix} xX + yY + zZ + wW \\ vapour \end{matrix}\right)\pi \quad \ldots\ldots \quad (9)$$

of which the pressure π and the composition of the mixture of vapours have been determined. It follows from the preceding that $\pi_x, \pi_y, \pi_z, \pi_w,$ etc. have been determined by the composition and the pressure P of the liquid L.

In (8^a) the pressure of the X-vapour on the membrane is π_x; therefore, in (9) the pressure of the X-vapour in the mixture of vapours must also be π_x; as this pressure is $x\pi$, it follows $x\pi = \pi_x$. If we compare system (9) besides with the systems (8^b), (8^c), (8^d), etc. then we find:

$$x\pi = \pi_x \quad ; \quad y\pi = \pi_y \quad ; \quad z\pi = \pi_z \quad ; \quad w\pi = \pi_w \quad \ldots \quad (10)$$

etc. As $x+y+z+w \ldots . 1$, follows:

$$\pi = \pi_x + \pi_y + \pi_z + \pi_w + \ldots\ldots \quad \ldots\ldots \quad (11)$$

so that π has been determined.

It appears from (9) that π is the pressure with which the liquid L presses the $(X+Y+Z+W\ldots.)$ vapour through the membrane; for this reason we call π the O. $(X+Y+Z+W\ldots.)$ *V.P.* or the total *O.V.P.* of the liquid. Then it appears from (11):

the total *O.V.P.* of a liquid is equal to the sum of the *O.V.P*'s of each of the components.

As π is known now, x, y, z, w etc. follow from (10), so the composition of the mixture of vapours in (9).

We now shall explain the above more in detail. The *O.X.A.* of a liquid with the composition:

$$x \; mol \; X + y \; mol \; Y + (1 - x - y) \; mol \; W \quad \ldots \quad (12)$$

has been determined by (comp. Gen. VI):

$$-\xi_x = \zeta + (1-x)\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \quad \ldots\ldots\ldots \quad (13)$$

If we have a liquid of the composition

$$a \; mol \; A + b \; mol \; B + c \; mol \; C + \ldots\ldots \quad \ldots\ldots \quad (14)$$

in which we take

$$a + b + c + \ldots = 1 \quad \ldots\ldots\ldots \quad (15)$$

then the *O.A.A.*, the *O.B.A.*, etc. have been determined by:

$$\left.\begin{aligned} -\xi_a &= \zeta + (1-a)\frac{\partial\zeta}{\partial a} - b\frac{\partial\zeta}{\partial b} - c\frac{\partial\zeta}{\partial c}\ldots \\ -\xi_b &= \zeta - a\frac{\partial\zeta}{\partial a} + (1-b)\frac{\partial\zeta}{\partial b} - c\frac{\partial\zeta}{\partial c}\ldots \end{aligned}\right\} \quad \ldots \quad (16)$$

etc. This also obtains for a vapour of the composition (14); if this obeys the gas-laws, we have:

$$\zeta = a\,Z_a + bZ_b + cZ_c + \ldots + RT\,[a \log a + b \log b + c \log c + \ldots] \quad (17)$$

If we calculate from this $\partial\zeta : \delta a$, $\delta\zeta : \partial b$, etc and if we take (15) into consideration, then we find:

$$\left.\begin{aligned} -\xi_{a.v} &= Z_a + RT \log a \\ -\xi_{b.v} &= Z_b + RT \log b \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (18)$$

etc. in which the index *v* indicates that these *O.A.*'s obtain for a vapour.

In the special case that the vapour consists of a single substance only (e.g. of *A*, then $a=1$ or of *B*, then $b=1$, etc.) follows from (18):

$$-\xi_{a.v} = Z_a \quad ; \quad -\xi_{b.v} = Z_b \,;\ \text{etc.} \quad \ldots\ldots\ldots \quad (19)$$

which may be seen at once.

We now begin by considering an osmotic equilibrium:

$$(aA + \ldots \textit{vapour})\ P \mid M(A) \mid (a_1A + \ldots \textit{vapour})\ P_1 \quad \ldots \quad (20)$$

in which a mixture of vapours containing the substance *A* is on both sides of the membrane *M*(*A*); the other substances may be the same as well as different. As the *O.A.A.* of both the mixtures of vapours must be equal, it follows from (18):

$$(Z_a)_P + RT \log a = (Z_a)_{P_1} + RT \log a_1 \quad \ldots\ldots \quad (21)$$

As $\dfrac{\partial Z}{\partial P} = V = \dfrac{RT}{P}$, we find:

$$(Z_a)_P - (Z_a)_{P_1} = \int_{P_1}^{P} \frac{RT}{P}\,dP = RT \log \frac{P}{P_1} \quad \ldots\ldots \quad (22)$$

Now it follows from (21)

$$RT \log P + RT \log a = RT \log P_1 + RT \log a_1 \quad \ldots \quad (23)$$

or:

$$aP = a_1P_1 \quad \ldots\ldots\ldots\ldots \quad (24)$$

So system (20) is in osmotic equilibrium when the pressure of the *A*-vapour is the same in both mixtures of vapours.

So in the special case that one of the vapour-phases consists of A-vapour only, the pressure of the A-vapour in the mixture of vapours must be equal to the pressure of the A-vapour. So if we have an osmotic-equilibrium

$$(aA + \ldots\ldots \mathit{vapour})\ P \mid M\,(A) \mid (A\text{-}\mathit{vapour})\ P_a \quad . \quad . \quad . \quad (25)$$

then it follows

$$aP = P_a$$

Between the pressure π in system (9) and the pressures π_x, π_y etc. in the systems (8) the relations (10) exist; it now follows from the above that the mixture of vapours of system (9) can be in osmotic equilibrium with each of the vapours of the systems (8).

In system (8^a) the $O.X.A.$ of the liquid is equal to the $O.X.A.$ of the vapour; as this consists of X-vapour only,

$$-(\xi_x)_P = (Z_x)_{\pi_x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26^a)$$

will obtain.

For the osmotic equilibria (8^b) etc. follows:

$$-(\xi_y)_P = (Z_y)_{\pi_y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26^b)$$

$$-(\xi_z)_P = (Z_z)_{\pi_z} \quad . \quad . \quad . \quad (26^c) \qquad -(\xi_w)_P = (Z_w)_{\pi_w} \quad . \quad . \quad . \quad (26^d)$$

etc. The membrane of system (9) is permeable for all substances; the $O.X.A.$, the $O.Y.A.$ etc. of the liquid must consequently be equal to that of the mixture of vapours. So for system (9) obtains:

$$\left.\begin{array}{l} -(\xi_x)_P = (Z_x)_\pi + RT \log x \quad ; \quad -(\xi_y)_P = (Z_y)_\pi + RT \log y \\ -(\xi_z)_P = (Z_z)_\pi + RT \log z \quad ; \quad -(\xi_w)_P = (Z_w)_\pi + RT \log w \end{array}\right\} \quad (27)$$

etc. From (26^a) and the first equation (27) follows:

$$(Z_x)_{\pi_x} = (Z_x)_\pi + RT \log x \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

We find from this $\pi_x = x\pi$. In a corresponding way we find also $\pi_y = y\pi$ etc. viz. the relations which have been mentioned already in (10).

If we change the pressure P in system (9), the composition of the liquid remaining constant, it follows from (27):

$$\left.\begin{array}{l} \triangle\, v_z \,.\, dP = V\,d\pi + \dfrac{RT}{x}\,dx \quad ; \quad \triangle\, v_y \,.\, dP = V\,d\pi + \dfrac{RT}{y}\,dy \\ \triangle\, v_z \,.\, dP = V\,d\pi + \dfrac{RT}{z}\,dz \quad ; \quad \triangle\, v_w \,.\, dP = V\,d\pi + \dfrac{RT}{w}\,dw \end{array}\right\} \quad (29)$$

etc. If we add these up, after having multiplied the first by x, the second by y, etc., bearing in mind that $x + y + \ldots\ldots = 1$, it follows:

$$d\pi = \frac{\triangle\, v_t}{V_\pi}\,dP \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

V_π is the volume of 1 grammol. of vapour under the pressure π and

$$\triangle v_t = x \triangle v_x + y \triangle v_y + z \triangle v_z + w \triangle v_w \,.$$

So $\triangle v_t \, dn$ is the increase of volume of the liquid, when this absorbs xdn quant. of X, ydn quant. of Y, etc. So, as $\triangle v_t$ is generally positive, it follows from (30):

if we increase the pressure P of a liquid, then π, viz. its total *O.V.P.* will increase.

This change in pressure is accompanied by a change dx, dy etc. of the mixture of vapours, which we can calculate from (29); a detailed consideration is left to the reader.

In the osmotic equilibrium

$$(L)\, P \mid M(W) \mid (W\text{-}vapour)\, \pi_w \quad \ldots\ldots \quad (31)$$

π_w has been determined by the composition and the pressure P of the liquid L. In paper I we have found the equation (19) for it; if we here give the index w to π and $\triangle v$, we get:

$$\log \pi_w = \log P_0 + \frac{P - P_0}{RT} \triangle v_w \quad \ldots\ldots \quad (32)$$

Here P_0 is the vapourpressure of the liquid L, therefore, the pressure under which te equilibrium:

$$(L + W\text{-}vapour)\, P_0 \quad \ldots\ldots \quad (33)$$

can exist, without the necessity of putting a membrane between both phases.

This shows it has been assumed that only one of the substances of L is volatile; if the liquid contains other volatile substances besides, e.g. X, Y, Z, W etc. then under the pressure P_0 we have the equlibrium:

$$[L + (x_0 X + y_0 Y + z_0 Z + w_0 W \ldots)\, vapour]\, P_0 \quad \ldots \quad (34)$$

in which x_0, y_0 etc. represent the composition of this mixture of vapours. We now must introduce a small change in (32) also; for this we follow the same way as in paper I.

As (31) is the same as (8^d), (26^d) obtains here; from this it follows (comp. Paper I):

$$\triangle v_w \,.\, dP = V d\pi_w = RT \frac{d\pi_w}{\pi_w} \quad \ldots\ldots \quad (35)$$

From this it follows:

$$\triangle v_w \,.\, P = RT \log \pi_w + C \quad \ldots\ldots \quad (36)$$

In order to determine the contstant C, we now take the liquid L under its own vapourpressure P_0. If the vapour only contains W-vapour, we consequently have the equilibrium (33). If a membrane $M(W)$ is put into it, we get the osmotic equilibrium;

$$(L)\,P_0 \mid M(W) \mid (W\text{-}vapour)\,P_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

in which the pressure is the same on both sides of the membrane.

So we also can satisfy (36) by $P = P_0$ and $\pi_w = P_0$; we then get:

$$\triangle v_w \,.\, P_0 = RT \log P_0 + C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Now (32) follows from (36) and (38).

When, however, the liquid L contains more volatile substances, then we have the equilibrium (34) under the pressure P_0; if a membrane $M(n)$ is put in, we get:

$$(L)\,P_0 \mid M(n) \mid \left(\underset{vapour}{x_0 X + y_0 Y + z_0 Z + w_0 W \ldots}\right) P_0 . \quad . \quad (39)$$

As the pressure of the W-vapour in the mixture of vapours is $w_0 P_0$, in the system

$$(L)\,P_0 \mid M(W) \mid (X\text{-}vapour)\, w_0 P_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

the pressure on the right side of the membrane must be $w_0 P_0$. So we now can satisfy (36) by $P = P_0$ and $\pi_w = w_0 P_0$; instead of (38) we then get:

$$\triangle v_w \,.\, P_0 = RT \log w_0 P_0 + C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

From (36) and (41) now follows:

$$\log \pi_w = \log w_0 P_0 + \frac{P_0 - P}{RT} \triangle v_w \quad . \quad . \quad . \quad . \quad . \quad (42^a)$$

or:

$$\log \pi_w = \log P_0 + \frac{P_0 - P}{RT} \triangle v_w + \log w_0 \quad . \quad . \quad . \quad . \quad (42^b)$$

If, therefore, we have a liquid of which more substances are volatile, then its $O.W.V.P.$ is no longer determined by (32), but by (42^a) or (42^b).

We may consider (32) as a special case of (42^a) or (42^b); when namely the vapour consists of W only, then $w_0 = 1$ and (42^a) and (42^b) pass into (32).

For an osmotic system

$$(L)\,P \mid M(W) \mid (L')\,P' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

we found in paper I the equation (22); if in this we give to π and π' the index w, we have, therefore:

$$(\xi_w)_P - (\xi'_w)_{P'} = RT \log \frac{\pi'_w}{\pi_w} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

Here ξ_w and ξ'_w are the $O.W.A.$, π_w and π'_w the $O.W.V.P.$ of the liquids L and L'.

As the direction in which the water diffuses through the membrane

depends upon the sign of the first part of (44) and, therefore, also upon that of the second part, it follows from this (comp. also Paper I):
the water diffuses through a membrane $M(W)$ towards that side, where the *O.W.V.P.* is smallest.

If we substitute the membrane $M(W)$ by a membrane $M(X)$, we have the system:

$$(L)\,P \mid M(X) \mid (L')\,P' \quad \ldots\ldots\ldots \quad (45)$$

For this obtains:

$$(\xi_x)_P - (\xi'_x)_{P'} = RT \log \frac{\pi'_x}{\pi_x} \quad \ldots\ldots\ldots \quad (46)$$

Consequently for the direction of the diffusion of the substance X the same obtains as above for the substance W. So we may say in general:

a substance S diffusses through a membrane $M(S)$ towards that side, where the *O.S.V.P.* is smallest.

We now take the osmotic system:

$$\left.\begin{array}{c} (L)\,P \mid M(n) \mid (L')\,P' \\ \longleftarrow \alpha X \;;\; \longleftarrow \beta Y \;;\; \longleftarrow \gamma Z \;;\; \longleftarrow \delta W \end{array}\right\} \;.\quad (47)$$

in which a membrane $M(n)$, so that all substances diffuse. We assume that α quant. of X, β quant. of Y etc. diffuse towards the left (when one of these quantities is negative, then the corresponding substance diffuses towards the right). As we have seen in Gen. VI, now α, β, γ etc. have to satisfy:

$$\alpha K_x + \beta K_y + \gamma K_z + \delta K_w \ldots\ldots > 0 \quad \ldots\ldots \quad (48)$$

The direction in which a substance runs through the membrane $M(n)$ is, therefore, no longer determined by the *O.A.* of that substance only, but by the *O.A.*'s of all substances together and by the nature of the membrane.

We now may also give an other form to (48). If we represent the *O.X.V.P.* the *O.Y.V.P.*, etc. of the liquid L by π_x, π_y etc. and those of the liquid L' by π'_x, π'_y etc., we have:

$$K_x = RT \log \frac{\pi'_x}{\pi_x} \quad ; \quad K_y = RT \log \frac{\pi'_y}{\pi_y} \;;\; \text{etc.} \quad \ldots \quad (49)$$

Substituting these values in (48), we find that α, β, γ etc. have to satisfy:

$$\left(\frac{\pi'_x}{\pi_x}\right)^{\alpha} \left(\frac{\pi'_y}{\pi_y}\right)^{\beta} \left(\frac{\pi'_z}{\pi_z}\right)^{\gamma} \left(\frac{\pi'_w}{\pi_w}\right)^{\delta} \ldots\ldots > 1 \quad \ldots\ldots \quad (50)$$

From this it follows among other things:

a substance X can diffuse through a membrane $M(n)$ from greater towards smaller-as well as from smaller towards greater *O.X.V.P.*

Of course the same obtains for the other substances.

Previously we have said:

a substance S passes congruently through a membrane, when it diffuses in the same direction as through a membrane $M(S)$; it diffuses incongruently when it runs through the membrane in opposite direction.

From this followed:

a substance S runs congruently through a membrane, when it diffuses from smaller towards greater- and incongruently when it diffuses from greater towards smaller $O.S.A.$

So now we may say also:

a substance S runs congruently through a membrane, when it diffuses from greater towards smaller- and incongruently when it diffuses from smaller towards greater $O.S.V.P.$

Leiden. *Lab. of Inorg. Chemistry.*

Mathematics. — *Bestimmung einer Körperbasis für die rationalen Invarianten einer quaternären in α und β alternierenden Grösse* $c_{\alpha\beta}^{\cdot\cdot\,\gamma}$. [1]) Von D. VAN DANTZIG. (Communicated by Prof. R. WEITZENBÖCK).

(Communicated at the meeting of April 27, 1929).

1. Die quaternäre alternierende Grösse $c_{\alpha\beta}^{\cdot\cdot\,\gamma} = -c_{\beta\alpha}^{\cdot\cdot\,\gamma}$ mit *unbestimmten* Bestimmungszahlen legt die folgenden Grössen fest:

erstens den kovarianten Vektor

$$c_\alpha = c_{\alpha\lambda}^{\cdot\cdot\,\lambda}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1$$

zweitens den kovarianten Tensor vom Rang 4

$$h_{\alpha\beta} = h_{\beta\alpha} = c_{\alpha\lambda}^{\cdot\cdot\,\mu}\, c_{\beta\mu}^{\cdot\cdot\,\lambda}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

drittens die kontravariante Tensordichte vom Rang 4 und vom Gewicht 1

$$\mathfrak{g}^{\alpha\beta} = \mathfrak{g}^{\beta\alpha} = 3\,!\; c_{[12}^{\cdot\cdot\,\alpha}\, c_{34]}^{\cdot\cdot\,\beta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

Daraus entstehen:

erstens die Affinordichte vom Rang 4, Gewicht 1 und Grad 4 (in den $c_{\alpha\beta}^{\cdot\cdot\,\gamma}$)

$$\mathfrak{M}_\alpha^{\cdot\,\beta} = h_{\alpha\lambda}\, \mathfrak{g}^{\lambda\beta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

zweitens die kovarianten Vektordichten

$$\overset{r}{\mathfrak{e}}_\alpha = \begin{cases} c_\alpha\,, & r = 1, \\ \mathfrak{M}_\alpha^{\cdot\,\lambda}\, \overset{r-1}{\mathfrak{e}}_\lambda\,, & r = 2, 3, 4, \end{cases} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

wo $\overset{i}{\mathfrak{e}}_\alpha$ $(i, j, \ldots = 1, 2, 3, 4)$ das Gewicht $i-1$ und den Grad $4\,i-3$ hat, und drittens die Unterdeterminanten dritten Grades $\underset{i}{\mathfrak{e}}^\alpha$ der Determinante $\mathfrak{D}$ der $\overset{i}{\mathfrak{e}}_\alpha$:

$$\sum_i \overset{i}{\mathfrak{e}}_\alpha\, \underset{i}{\mathfrak{e}}^\beta = \mathfrak{D} A_\alpha^\beta = \begin{cases} \mathfrak{D}, & \alpha = \beta, \\ 0, & \alpha \neq \beta, \end{cases} \qquad \overset{i}{\mathfrak{e}}_\lambda\, \underset{j}{\mathfrak{e}}^\lambda = \mathfrak{D}\delta_j^i = \begin{cases} \mathfrak{D}, & i = j \\ 0, & i \neq j \end{cases} \quad . \quad . \qquad (6)$$

$\mathfrak{D}$ ist eine relative Invariante vom Rang 4, Gewicht 7 und Grad 28; $\underset{i}{\mathfrak{e}}^\alpha$ ist eine kontravariante Vektordichte vom Gewicht $8-i$ und vom Grad $31-4\,i$.

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[1]) Veranlassung zu dieser Note gab eine Bemerkung von R. WEITZENBÖCK: Differentialinvarianten in der EINSTEINschen Theorie des Fernparallelismus, Berliner Sitzungsberichte (1928), S. 471.

Setzt man jetzt

$$\overset{k}{\underset{ij}{\mathfrak{c}}} = -\overset{k}{\underset{ji}{\mathfrak{c}}} = c_{\alpha\beta}^{\cdot\cdot\gamma}\, \underset{i}{\mathfrak{e}}^{\alpha}\, \underset{j}{\mathfrak{e}}^{\beta}\, \overset{k}{\mathfrak{e}}_{\gamma}, \quad \ldots\ldots\ldots \quad (7)$$

so ist $\overset{k}{\underset{ij}{\mathfrak{c}}}$ eine relative Invariante vom Gewicht $15-(i+j-k)$ und vom Grad $60-4(i+j-k)$. Weil, wie wir sogleich beweisen werden, bei unbestimmten Bestimmungszahlen $\mathfrak{D} \neq 0$ ist, wird

$$c_{\alpha\beta}^{\cdot\cdot\gamma} = \frac{\sum\limits_{ijk} \overset{k}{\underset{ij}{\mathfrak{c}}}\, \overset{i}{\mathfrak{e}}_{\alpha}\, \overset{j}{\mathfrak{e}}_{\beta}\, \underset{k}{\mathfrak{e}}^{\gamma}}{\mathfrak{D}^3} \quad \ldots\ldots\ldots \quad (8)$$

Hieraus ergibt sich sofort, dass die 25 Invarianten $\overset{k}{\underset{ij}{\mathfrak{c}}}$ und $\mathfrak{D}$ die gesuchte Körperbasis bilden.[1] [2] Denn eine beliebige rationale Invariante der $c_{\alpha\beta}^{\cdot\cdot\gamma}$ lässt sich, mit Koeffizienten, die von den $\overset{k}{\underset{ij}{\mathfrak{c}}}$ und $\mathfrak{D}$ abhängen, als eine rationale Invariante der $\overset{i}{\mathfrak{e}}_{\alpha}$ und $\underset{i}{\mathfrak{e}}^{\alpha}$ ausdrücken; eine solche gibt es aber nicht ausser $\mathfrak{D}$.[3]

2. Um zu beweisen, dass für unbestimmte Bestimmungszahlen $\mathfrak{D} \neq 0$ ist, genügt es, eine Spezialisierung nach bestimmten Bestimmungszahlen anzugeben, für die $\mathfrak{D} \neq 0$ ist. Dazu bezeichne $\bar{i}$ bzw. $\underline{i}$ den i-ten kontravarianten bzw. kovarianten Massvektor in einem beliebigen Koordinatensystem (also $\underset{i}{e}^{\alpha}$ bzw. $\overset{i}{e}_{\alpha}$), $\bar{i}\,\bar{j}$, $\bar{i}\,\underline{j}$, $\underline{i}\,\bar{j}$ und $\underline{i}\,\underline{j}$ das allgemeine Produkt von zwei solchen Vektoren ($\underset{i}{e}^{\alpha}\,\underset{j}{e}^{\beta}$, usw.); Zahlen ohne Querstrich sind gewöhnliche Zahlenfaktoren. Setzt man dann für

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[1] Praktisch leistet sie wenig, weil $\mathfrak{D}$ in den einfachsten Fällen verschwindet. Z.B. verschwindet im gruppentheoretischen Fall, wo $c_{[\alpha\beta}^{\cdot\cdot\lambda}\, c_{\gamma]\lambda}^{\cdot\cdot\delta} = 0$ ist, $g^{\alpha\beta} c_{\beta}$, folglich auch $\overset{2}{\mathfrak{e}}_{\alpha}$ und $\mathfrak{D}$.

[2] Eine (ganze rationale) Basis für diejenigen ganzen rationalen Invarianten der quaternären alternierenden Grösse $c^{\alpha\beta}_{\cdot\cdot\gamma}$, deren Grade $\leqq 8$ sind, ist von I. C. CHOUFOER aufgestellt worden (Het punt-lijn-connex in de driedimensionale ruimte, Diss., Amsterdam, 1927). Die hier aufgestellte Körperbasis aller rationalen Invarianten enthält solche bis zum 64-ten Grade.

[3] Die $\overset{k}{\underset{ij}{\mathfrak{c}}}$ sind bis auf geeignete Potenzen von $\mathfrak{D}$ die Bestimmungszahlen von $c_{\alpha\beta}^{\cdot\cdot\gamma}$ bzgl. eines invariant definierten Koordinatensystems, dessen Massvektoren bis auf geeignete Potenzen von $\mathfrak{D}$ die $\overset{i}{\mathfrak{e}}_{\alpha}$ und $\underset{i}{\mathfrak{e}}^{\alpha}$ sind. Vgl. auch G. F. C. GRISS, Differentialinvarianten von Systemen von Vektoren, Diss. Amsterdam (1925), S. 32.

$$c_{\alpha\beta}^{\cdot\cdot\gamma} \quad (\underline{1}\,\underline{3}-\underline{3}\,\underline{1})\,\bar{1}+(\underline{2}\,\underline{4}-\underline{4}\,\underline{2})\,\bar{2}+(\underline{4}\,\underline{1}-\underline{1}\,\underline{4})\,(\bar{3}+\bar{4})+(\underline{2}\,\underline{3}-\underline{3}\,\underline{2})\,(\bar{3}-\bar{4}),$$

so wird

$$h_{\alpha\beta} \quad \underline{1}\,\underline{1}+(\underline{1}\,\underline{2}+\underline{2}\,\underline{1})+\underline{2}\,\underline{2}+(\underline{1}\,\underline{4}+\underline{4}\,\underline{1})+(\underline{2}\,\underline{3}+\underline{3}\,\underline{2})+\underline{3}\,\underline{3}+\underline{4}\,\underline{4},$$

$$\mathfrak{g}^{\alpha\beta} \quad -(\bar{1}\,\bar{2}+\bar{2}\,\bar{1})-2\,\bar{3}\,\bar{3}-2\,\bar{4}\,\bar{4},$$

$$\mathfrak{M}_{\alpha}^{\cdot\beta} \quad -(\underline{1}+\underline{2}+\underline{3})\,\bar{1}-(\underline{1}+\underline{2}+\underline{4})\,\bar{2}-2\,(\underline{2}+\underline{3})\,\bar{3}-2\,(\underline{1}+\underline{4})\,\bar{4},$$

$$\overset{1}{\mathfrak{e}}_{\alpha}=c_{\alpha} \quad -\underline{1}+\underline{2}-\underline{3}-\underline{4},$$

$$\overset{2}{\mathfrak{e}}_{\alpha} \quad 2\,\underline{1}+2\,\underline{2}+3\,\underline{3}+\underline{4},$$

$$\overset{3}{\mathfrak{e}}_{\alpha} \quad -6\,\underline{1}-10\,\underline{2}-8\,\underline{3}-4\,\underline{4},$$

$$\overset{4}{\mathfrak{e}}_{\alpha} \quad 24\,\underline{1}+32\,\underline{2}+22\,\underline{3}+18\,\underline{4},$$

und

$$\mathfrak{D}=64\neq 0.$$

3. Substitution von (8) in (1) und (5) ergibt 4 Relationen ersten und 12 Relationen vierten Grades in den $\overset{k}{\underset{ij}{\mathfrak{c}}}$ zwischen diesen Invarianten und $\mathfrak{D}$. Dies stimmt überein mit der zu erwartenden Anzahl von $24-16=8$ absoluten, also 9 relativen algebraisch unabhängigen Invarianten. Die Relationen lauten:

$$\sum_{j}\overset{j}{\underset{ij}{\mathfrak{c}}}=\begin{cases}\mathfrak{D}^2, & i=1,\\ 0, & i\neq 1,\end{cases} \quad \ldots\ldots\ldots \tag{9}$$

$$3!\sum_{jkl}\overset{k}{\underset{il}{\mathfrak{c}}}\,\overset{l}{\underset{jk}{\mathfrak{c}}}\,\overset{j}{\underset{[12}{\mathfrak{c}}}\,\overset{m}{\underset{34]}{\mathfrak{c}}}=\begin{cases}\mathfrak{D}^7, & i=m+1,\quad m=1,2,3,\\ 0, & i\neq m+1,\quad m=1,2,3.\end{cases} \quad \ldots \tag{10}$$

Mathematics. — *Bestimmung einer Körperbasis für die rationalen Invarianten einer allgemeinen n-ären Grösse* $c_{\alpha\beta}^{\cdot\cdot\,\gamma}$. Von D. VAN DANTZIG. (Communicated by Prof. R. WEITZENBÖCK).

(Communicated at the meeting of April 27, 1929).

1. Die allgemeine n-äre Grösse $c_{\alpha\beta}^{\cdot\cdot\,\gamma}$ mit *unbestimmten* Bestimmungszahlen legt die folgenden Grössen fest:
erstens den kovarianten Vektor

$$c_\alpha = c_{\alpha\lambda}^{\cdot\cdot\,\lambda}, \quad \ldots \ldots \ldots \quad (1)$$

zweitens die kovariante Grösse zweiten Grades vom Rang n

$$k_{\alpha\beta} = c_{\alpha\beta}^{\cdot\cdot\,\lambda}\, c_\lambda, \quad \ldots \ldots \ldots \quad (2)$$

und drittens den kovarianten Tensor zweiten Grades vom Rang n

$$h_{\alpha\beta} = h_{\beta\alpha} = c_{\alpha\lambda}^{\cdot\cdot\,\mu}\, c_{\beta\mu}^{\cdot\cdot\,\lambda} \quad \ldots \ldots \ldots \quad (3)$$

Es sei $\mathfrak{h}^{\alpha\beta}$ die kovariante Tensordichte vom Gewicht 2 und vom Grad $2n-2$ in den $c_{\alpha\beta}^{\cdot\cdot\,\gamma}$, deren Bestimmungszahlen die Unterdeterminanten $(n-1)$-ten Grades der Determinante $\mathfrak{h}$ der $h_{\alpha\beta}$ sind:

$$h_{\alpha\lambda}\, \mathfrak{h}^{\lambda\beta} = \mathfrak{h}\, A_\alpha^\beta = \begin{cases} \mathfrak{h}, & \alpha = \beta, \\ 0, & \alpha \neq \beta. \end{cases}$$

Es ergeben sich dann:
erstens die Affinordichte vom Gewicht 2 und vom Grad $2n$

$$\mathfrak{P}_\alpha^{\cdot\,\beta} = k_{\alpha\lambda}\, \mathfrak{h}^{\lambda\beta}, \quad \ldots \ldots \ldots \quad (4)$$

zweitens die kovarianten Vektordichten

$$\overset{r}{\mathfrak{v}}_\alpha = \begin{cases} c_\alpha, & r = 1, \\ \mathfrak{P}_\alpha^{\cdot\,\lambda}\, \overset{r-1}{\mathfrak{v}}_\lambda, & r = 2, 3, \ldots, n, \end{cases} \quad \ldots \ldots \quad (5)$$

wo $\overset{i}{\mathfrak{v}}_\alpha$ $(i, j, \ldots = 1, \ldots, n)$ das Gewicht $2\,i-2$ und den Grad $2n\,(i-1)+1$ hat, und drittens die Unterdeterminanten $(n-1)$-ten Grades $\underset{i}{\mathfrak{v}}^\alpha$ der Determinante $\mathfrak{B}$ der $\overset{i}{\mathfrak{v}}_\alpha$:

$$\sum_i \overset{i}{\mathfrak{v}}_\alpha\, \underset{i}{\mathfrak{v}}^\beta = \mathfrak{B}\, A_\alpha^\beta\,; \qquad \underset{i}{\mathfrak{v}}^\alpha\, \overset{j}{\mathfrak{v}}_\alpha = \mathfrak{B}\, \delta_i^j = \begin{cases} \mathfrak{B}, & i = j, \\ 0, & i \neq j. \end{cases} \quad \ldots \quad (6)$$

$\mathfrak{B}$ ist eine relative Invariante vom Rang n, Gewicht n^2-n+1 und Grad $n\,(n^2-n+1)$; $\underset{i}{\mathfrak{v}}^\alpha$ ist eine kontravariante Vektordichte vom Gewicht $n^2-n+3-2i$ und vom Grad $n\,(n^2-n+3-2i)-1$.

Setzt man jetzt

$$\overset{k}{\underset{ij}{\mathfrak{C}}} = c_{\alpha\beta}^{\cdot\cdot\gamma}\, \underset{i}{\mathfrak{v}}^{\alpha}\, \underset{j}{\mathfrak{v}}^{\beta}\, \overset{k}{\mathfrak{v}}_{\gamma}, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (7)$$

so ist $\overset{k}{\underset{ij}{\mathfrak{C}}}$ eine relative Invariante vom Gewicht $2\{n^2-n+2)-(i+j-k)\}$ und vom Grad $2n\{(n^2-n+2)-(i+j-k)\}$.

Weil, wie wir sogleich beweisen werden, bei unbestimmten Bestimmungszahlen $\mathfrak{V} \neq 0$ ist, wird:

$$c_{\alpha\beta}^{\cdot\cdot\gamma} = \frac{\sum\limits_{ijk} \overset{k}{\underset{ij}{\mathfrak{C}}}\, \overset{i}{\mathfrak{v}}_{\alpha} \overset{j}{\mathfrak{v}}_{\beta} \underset{k}{\mathfrak{v}}^{\gamma}}{\mathfrak{V}^3} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (8)$$

Hieraus ergibt sich sofort, dass die n^3+1 Invarianten $\overset{k}{\underset{ij}{\mathfrak{C}}}$ und $\mathfrak{V}$ die gesuchte Körperbasis bilden [1]). Denn eine beliebige rationale Invariante der $c_{\alpha\beta}^{\cdot\cdot\gamma}$ lässt sich, mit Koeffizienten, die von den $\overset{k}{\underset{ij}{\mathfrak{C}}}$ und $\mathfrak{V}$ abhängen, als eine rationale Invariante der $\overset{i}{\mathfrak{v}}_{\alpha}$ und $\underset{i}{\mathfrak{v}}^{\alpha}$ ausdrücken; eine solche gibt es aber nicht ausser $\mathfrak{V}$ [2]).

2. Um zu beweisen, dass für unbestimmte Bestimmungszahlen $\mathfrak{V} \neq 0$ ist, genügt es, eine spezielle Grösse anzugeben, für die $\mathfrak{V} \neq 0$ ist. Dazu betrachten wir eine n-äre Grösse $c_{\alpha\beta}^{\cdot\cdot\gamma}$, die sich additiv in zwei Grössen $c'^{\cdot\cdot\gamma}_{\alpha\beta}$ und $c''^{\cdot\cdot\gamma}_{\alpha\beta}$ zerlegen lässt, von denen die erste nur nach m unabhängigen Richtungen, und die zweite nur nach $n-m$ von diesen und von einander unabhängigen Richtungen nicht-verschwindende Komponenten hat, sodass jede Überschiebung von $c'^{\cdot\cdot\gamma}_{\alpha\beta}$ mit $c''^{\cdot\cdot\gamma}_{\alpha\beta}$ verschwindet. Eine jede der oben eingeführten Grössen wird dann in ebensolcher Weise additiv zerlegt; insbesondere wird

$$\mathfrak{P}_{\alpha}^{\cdot\beta} = \mathfrak{h}''\, \mathfrak{P}'^{\cdot\beta}_{\alpha} + \mathfrak{h}'\, \mathfrak{P}''^{\cdot\beta}_{\alpha}$$

$$\overset{i}{\mathfrak{v}}_{\alpha} = (\mathfrak{h}'')^{i-1}\, \overset{i}{\mathfrak{v}}'_{\alpha} + (\mathfrak{h}')^{i-1}\, \overset{i}{\mathfrak{v}}''_{\alpha}$$

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[1]) Praktisch leistet sie wenig, weil $\mathfrak{V}$ in den einfachsten Fällen verschwindet. Z.B. ist im gruppentheoretischen Fall, wo $c_{[\alpha\beta}^{\cdot\cdot\lambda}\, c_{\gamma]\lambda}^{\cdot\cdot\mu} = 0$ ist, $k_{\alpha\beta} = 0$, und im von R. WEITZENBÖCK (Ueber einen gemischten Tensor A^{λ}_{ik}, Monatshefte für M. & Ph., **35** (1928) 1—8) erledigten Fall des kommutativen assoziativen Zahlensystems $h_{\alpha\beta} = k_{\alpha\beta}$, folglich $\overset{i}{\mathfrak{v}}_{\alpha} = \mathfrak{h}^{i-1} c_{\alpha}$; in den beiden Fällen ist also $\mathfrak{V} = 0$.

[2]) Die $\overset{k}{\underset{ij}{\mathfrak{C}}}$ sind bis auf geeignete Potenzen von $\mathfrak{V}$ die Bestimmungszahlen von $c_{\alpha\beta}^{\cdot\cdot\gamma}$ bzgl. eines invariant definierten Koordinatensystems, dessen Massvektoren bis auf geeignete Potenzen von $\mathfrak{V}$ die $\overset{i}{\mathfrak{v}}_{\alpha}$ und $\underset{i}{\mathfrak{v}}^{\alpha}$ sind. Vgl. auch G. F. C. GRISS, Differentialinvarianten von Systemen von Vektoren, Diss. Amsterdam (1925), S. 32.

wo $\mathfrak{h}'$ bzw. $\mathfrak{h}''$ der Elementarteiler m-ten bzw. $(n-m)$-ten Grades der Matrix $h'_{\alpha\beta}$ bzw. $h''_{\alpha\beta}$ ist, und wo $\overset{i}{\mathfrak{v}}{}'_{\alpha}$ bzw. $\overset{i}{\mathfrak{v}}{}''_{\alpha}$ die $(i-1)$-te Transformierte mittels $\mathfrak{P}'^{\cdot\beta}_{\alpha}$ bzw. $\mathfrak{P}''^{\cdot\beta}_{\alpha}$ von c'_{α} bzw. c''_{α} ist. $\mathfrak{V}$ wird dann bis auf Potenzen von $\mathfrak{h}'$, $\mathfrak{h}''$, $\overset{m}{\mathfrak{V}'} = \overset{1}{\mathfrak{v}}{}'_{[1} \dots \overset{m}{\mathfrak{v}}{}'_{m]}$ und $\overset{n-m}{\mathfrak{V}''} = \overset{1}{\mathfrak{v}}{}''_{[1} \dots \overset{n-m}{\mathfrak{v}}{}''_{n-m]}$ einer Simultaninvariante von $\mathfrak{P}'^{\cdot\beta}_{\alpha}$ und $\mathfrak{P}''^{\cdot\beta}_{\alpha}$ gleich, die nicht identisch verschwindet, wie sich zeigt, wenn man, weitergehend, $c'^{\cdot\cdot\gamma}_{\alpha\beta}$ und $c''^{\cdot\cdot\gamma}_{\alpha\beta}$ in solcher Weise spezialisiert, dass $\overset{m+1}{\mathfrak{v}}{}'_{\alpha} = \overset{1}{\mathfrak{v}}{}'_{\alpha}$ und $\overset{n-m+1}{\mathfrak{v}}{}''_{\alpha} = 0$ wird.

Für $n=2$ und $n=3$ lassen sich leicht Grössen mit nicht verschwindendem $\mathfrak{V}$ angeben (auch für $n=1$, aber das genügt nicht, weil für $m=n-m=1$ die Simultaninvariante von $\mathfrak{P}'^{\cdot\beta}_{\alpha}$ und $\mathfrak{P}''^{\cdot\beta}_{\alpha}$ identisch verschwindet); folglich gibt es solche Grössen für beliebiges n.

Weitergehend ergibt sich genau so, dass auch für die allgemeine n-äre *symmetrische* Grösse $c^{\cdot\cdot\gamma}_{\alpha\beta}$ $\mathfrak{V} \neq 0$ ist. Ist $c^{\cdot\cdot\gamma}_{\alpha\beta}$ *alternierend* in α und β, so verschwindet $\mathfrak{V}$ identisch für $n \leqq 4$. Für $n=4$ führt die in der vorstehenden Note definierte Grösse mit den dortigen Bezeichnungen auf

$k_{\alpha\beta}$ $\quad (\underline{3} - 2\,\underline{4})\,\underline{1} - \underline{4}\,\underline{2} - \underline{1}\,\underline{3} + (2\,\underline{1} + \underline{2})\,\underline{4}$

$\mathfrak{h}^{\alpha\beta}$ $\quad \bar{1}\,(\bar{2} - \bar{3}) + \bar{2}\,(\bar{1} - \bar{4}) + \bar{3}\,(-\bar{1} + \bar{3} + \bar{4}) + \bar{4}\,(-\bar{2} + \bar{3} + \bar{4})$

$\mathfrak{P}^{\cdot\beta}_{\alpha}$ $\quad (\underline{1} - \underline{4})\,\bar{1} - (2\,\underline{1} + \underline{2} - \underline{3} + 2\,\underline{4})\,\bar{2} + (\underline{1} + \underline{2} - \underline{3} + 2\,\underline{4})\,\bar{3} + (\underline{1} + \underline{2} + \underline{4})\,\bar{4}$

$\overset{1}{\mathfrak{v}}_{\alpha} = c_{\alpha}$ $\quad -\underline{1} + \underline{2} - \underline{3} - \underline{4}$

$\overset{2}{\mathfrak{v}}_{\alpha}$ $\quad -5\,\underline{1} - 3\,\underline{2} + 2\,\underline{3} - 4\,\underline{4}$

$\overset{3}{\mathfrak{v}}_{\alpha}$ $\quad -\underline{1} + \underline{2} - 5\,\underline{3} + 11\,\underline{4}$

$\overset{4}{\mathfrak{v}}_{\alpha}$ $\quad 3\,\underline{1} + 5\,\underline{2} + 6\,\underline{3}$

und

$$\mathfrak{V} = -896 \neq 0.$$

Hiermit ist also eine zweite [1] Körperbasis für die rationalen Invarianten der alternierenden quaternären Grösse $c^{\cdot\cdot\gamma}_{\alpha\beta}$ gefunden. Wenigstens für jedes durch 4 teilbare n ist also das Nichtverschwinden von $\mathfrak{V}$ bei der allgemeinen alternierenden Grösse gesichert. Für ungerades n dagegen verschwindet $\mathfrak{V}$ identisch, weil dann der Rang von $k_{\alpha\beta}$, folglich auch von $\mathfrak{P}^{\cdot\beta}_{\alpha}$ kleiner als n ist. Ob dies auch für $n \equiv 2 \pmod{4}$ zutrifft, bleibe dahingestellt.

3. Substitution von (8) in (1) und (5) ergibt n Relationen ersten und $n(n-1)$ Relationen $2n$-ten Grades in den $\overset{k}{\underset{ij}{\mathfrak{E}}}$ zwischen diesen Inva-

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[1] Vgl. die vorangehende Note. Die dort definierte Körperbasis besteht aus Invarianten niedrigeren Grades, lässt sich aber nicht auf beliebiges n erweitern.

rianten und $\mathfrak{V}$. Dies stimmt überein mit der zu erwartenden Anzahl von n^3-n^2 absoluten, also n^3-n^2+1 relativen algebraisch unabhängigen Invarianten. Die Relationen lauten:

$$\sum_j \overset{j}{\underset{ij}{\mathfrak{C}}} = \begin{cases} \mathfrak{V}^2, & i=1, \\ 0, & i \neq 1. \end{cases} \quad \dots\dots\dots \quad (9)$$

$$n!^2 \sum_{\substack{i_1\dots i_n,\, k \\ j_1\dots j_n,\, l}} \overset{l}{\underset{kl}{\mathfrak{C}}}\ \overset{k}{\underset{i_1[1}{\mathfrak{C}}}\ \overset{j_2}{\underset{2|i_2|}{\mathfrak{C}}}\ \overset{j_3}{\underset{3|i_3|}{\mathfrak{C}}} \dots \overset{j_n}{\underset{n]\,i_n}{\mathfrak{C}}}\ \delta^{j_1}_{[1}\ \overset{i_2}{\underset{2|j_2|}{\mathfrak{C}}}\ \overset{i_3}{\underset{3|j_3|}{\mathfrak{C}}} \dots \overset{i_n}{\underset{n]\,j_n}{\mathfrak{C}}} = \mathfrak{V}^{4n-2}\delta^{j_1+1}_{i_1}. \quad (10)$$

Mathematics. — M. J. VAN UVEN: *Scheeve correlatie tusschen twee veranderlijken.* (Communicated by Prof. A. A. NIJLAND).

(Communicated at the meeting of April 27, 1929).

In het artikel „Over het bewerken van Scheeve Correlatie" (Versl. K. A. v. W. **34**, pp. 787 en 965; **35**, p. 129) hebben we getracht uit een willekeurige frequentieverdeeling van twee veranderlijken, x en x', een normale verdeeling te construeeren van twee (unimodulaire) veranderlijken t en t', die zoo eenvoudig mogelijk van x en x' afhangen. De aldaar ontwikkelde methode kan zeer beknopt worden samengevat als volgt:

De frequentieverdeeling is gegeven door:

Voor Y_{kl} exemplaren geldt:

$$x_{k-1} < x < x_k,\ x'_{l-1} < x' < x'_l \ (k=1,\ldots n;\ l=1,\ldots n';\ \sum_{k=1}^{n}\sum_{l=1}^{n'} Y_{kl}=N)$$

Als hulpfuncties voeren we in:

$z(x)$, waarbij $z_k = z(x_k)$ bepaald wordt door

$$\Theta(z_k) = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{z_k} e^{-v^2}\,dv = s_k = \frac{\sum\limits_{i=1}^{k}\sum\limits_{j=1}^{n'} Y_{ij}}{N},$$

$z'(x')$, waarbij $z'_l = z'(x'_l)$ bepaald wordt door

$$\Theta(z'_l) = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{z'_l} e^{-v^2}\,dv = s'_l = \frac{\sum\limits_{i=1}^{n}\sum\limits_{j=1}^{l} Y_{ij}}{N},$$

$\zeta(x, x')$, waarbij $\zeta_{k-1/2,\,l} = \zeta(x_{k-1/2}, x'_l)$ bepaald wordt door

$$\Theta(\zeta_{k-1/2,\,l}) = \sigma_{k-1/2,\,l} = \frac{\sum\limits_{j=1}^{l} Y_{kj}}{\sum\limits_{j=1}^{n'} Y_{kj}},$$

$\zeta'(x, x')$, waarbij $\zeta'_{k,\,l-1/2} = \zeta'(x_k, x'_{l-1/2})$ bepaald wordt door

$$\Theta(\zeta'_{k,\,l-1/2}) = \sigma'_{k,\,l-1/2} = \frac{\sum\limits_{i=1}^{k} Y_{il}}{\sum\limits_{i=1}^{n} Y_{il}}.$$

De differentiaal-kansformule luidt nu:

$$dW = \frac{\sqrt{1-\gamma^2}}{\pi} e^{-(t^2-2\gamma t\, t'-t'^2)}\, dt\, dt' \rightleftarrows e^{-(z^2+\zeta^2)} \frac{\partial \zeta}{\partial z'} dz\, dz' = \frac{1}{\pi} e^{-(z'^2+\zeta'^2)} \frac{\partial \zeta'}{\partial z} dz\, dz'.$$

Door

$$\gamma = \cos\omega,\ z^2+\zeta^2 = r^2,\ z'^2+\zeta'^2 = r'^2,\ zz'-\zeta\zeta' = A,\ z\zeta'+z'\zeta = B$$

te stellen krijgen we

$$\gamma = \cos\omega = \frac{A}{rr'},\ \sqrt{1-\gamma^2} = \sin\omega = \frac{B}{rr'}.$$

Voeren we nu twee rechthoekige (tegengesteld georiënteerde) coördinaatstelsels (z, ζ), (z', ζ') in, zóó, dat $\angle(z, z') = \omega$, dan wordt het stel z, ζ afgebeeld door een punt P en het stel z', ζ' door een punt P', zóó, dat OP' langs OP valt (fig. 1).

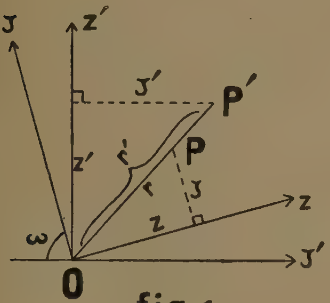

fig. 1

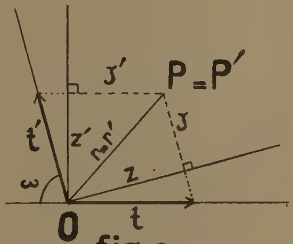

fig. 2

Wanneer nu in elk stel x_k, x'_l gevonden wordt:

I. $r' = r$, zoodat P' met P samenvalt (fig. 2),

II. $\operatorname{tg}\omega = \frac{B}{A} =$ constant, zoodat de hoek ω bij elk stel x, x' even groot uitvalt, dan blijkt er lineaire correlatie te bestaan tusschen de (unimodulaire) functies

$$t = \frac{z(x)}{\sin\omega} \quad \text{en} \quad t' = \frac{z'(x')}{\sin\omega},$$

terwijl de correlatiecoëfficient is: $\gamma = \cos\omega$ (Versl. K. A. v. W. **34**, p. 978). Is er *wel* voldaan aan $r' = r$, terwijl daarentegen ω veranderlijk blijkt te zijn, dan kunnen we een constanten hoek $\bar{\omega}$ (bij voorkeur een gemiddelde waarde van de veranderlijke ω) invoeren en het stelsel (z', ζ') vervangen door een stelsel $(\bar z', \bar\zeta')$ zóódanig, dat $\angle (z, \bar z') = \bar\omega$ (fig. 3).

Daarmee hebben we dan lineaire correlatie tot stand gebracht tusschen de (unimodulaire) functies

$$\bar t = \frac{z(x)}{\sin \bar\omega} \quad \text{en} \quad \bar t' = \zeta + \cot \bar\omega \,.\, z,$$

met correlatiecoëfficient $\bar\gamma = \cos \bar\omega$.

Daar $\zeta = \dfrac{z' - \cos \omega \,.\, z}{\sin \omega}$, hebben we

$$\bar t' = (\cot \bar\omega - \cot \omega)\, z + \frac{z'}{\sin \omega} =$$

$$= \frac{\sin (\omega - \bar\omega)}{\sin \omega \,.\, \sin \bar\omega} \,.\, z + \frac{z'}{\sin \omega},$$

conform met verg. (42) l.c. p. 981.

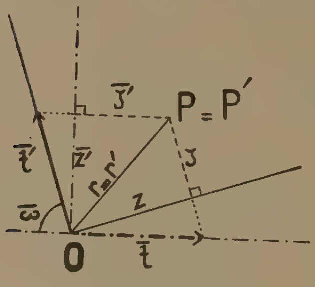

fig. 3

Terwijl $\bar t$ nu een zuivere functie is van x, is $\bar t'$ een gemengde functie van x en x' (zie ook de uitspraak op p. 982 l.c.).

Is evenmin voldaan aan $r' = r$, dan kunnen we P en P' tot één enkel punt P^* herleiden. Men past dus als het ware een vereffeningsmethode toe, die tusschen de twee verschillende punten een compromis sluit. In het aangehaalde artikel hebben we voor dit „vereffeningspunt" P^* gekozen: het op OPP' gelegen punt P^*, waarvoor $OP^* = R = \sqrt{rr'}$ (verg. Versl. K. A. v. W. **35**, p. 129). Daardoor werden zoowel z als z' aangetast; en het resultaat was, dat de unimodulaire veranderlijken t en t' beide gemengde functies werden van x en x'. Vandaar de uitspraak op p. 130 l.c. Wel is waar werd (zie de noot op p. 130 l.c.) de theoretische mogelijkheid erkend één der veranderlijken t en t' tot een zuivere functie van x (of x') te maken, maar het werd betwijfeld, of deze theoretische oplossing practische beteekenis zou hebben.

Het is ons intusschen gebleken, dat men ook in het algemeenste geval $(r' \neq r)$ zeer eenvoudig een zoodanige oplossing (bijv.: $t(x)$, $t'(x, x')$) kan construeeren.

Opdat t een zuivere functie zij van x, hebben we slechts:

1⁰. een constanten hoek $\bar\omega$ in te voeren,

2⁰. de functie $z(x)$ ongewijzigd te laten.

Van de ontelbare manieren, waarop we een dergelijke oplossing kunnen verkrijgen, noemen we er twee, die o. i. bijzonder de aandacht verdienen.

a. We behouden z en z'; de punten P en P' worden dan verplaatst naar een punt P^*, waarvoor $z^* = z$, $z'^* = z'$ (fig. 4). Daarbij veranderen natuurlijk ζ en ζ'. ζ gaat over in

$$\zeta^* = \frac{z' - \cos \omega \,.\, z}{\sin \omega} = - \cot \omega \,.\, z + \frac{z'}{\sin \omega}.$$

De hoek ω wordt ook hier ontleend aan

$$\operatorname{tg}\omega = \frac{B}{A} = \frac{z\zeta' + z'\zeta}{zz' - \zeta\zeta'};$$

ζ en ζ' werken dus nog mede tot het bepalen van ω.

Voeren we nu nog den constanten hoek $\bar\omega$ in (zie boven), dan komen

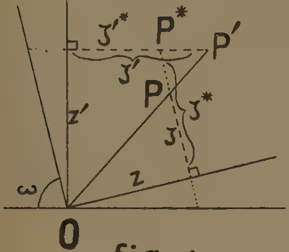

fig. 4

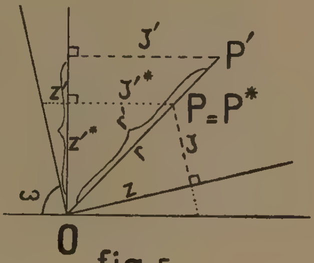

fig. 5

we tot de unimodulaire functies:

$$\bar t = \frac{z}{\sin\bar\omega}, \bar t^{*} = \zeta^{*} + \cot\bar\omega \,.\, z = (\cot\bar\omega - \cot\omega)\,.\,z + \frac{z'}{\sin\omega} =$$

$$= \frac{\sin(\omega - \bar\omega)}{\sin\omega \,.\, \sin\bar\omega}\,.\,z + \frac{z'}{\sin\omega},$$

dus tot dezelfde functies $(\bar t, \bar t')$ als in het geval $r' = r$.

b. We behouden z en ζ, d. w. z. we geven P' geheel prijs (of, anders gezegd: P' wordt vereffend tot P) (fig. 5). De coördinaten z' en ζ' van P' dienen nu alleen ter bepaling van den hoek ω. De functies z' en ζ' gaan nu resp. over in

$$z'^{*} = \frac{r}{r'}\,.\,z', \quad \zeta'^{*} = \frac{r}{r'}\,.\,\zeta'.$$

z'^{*} wordt zoodoende een gemengde functie van x en x'.

Invoering van den constanten hoek $\bar\omega$ brengt ons dan tot de unimodulaire functies

$$\bar t = \frac{z}{\sin\bar\omega}, \quad \bar t'^{*} = \zeta + \cot\bar\omega\,.\,z.$$

Hier geldt

$$\zeta = \frac{z'^{*} - \cos\omega\,.\,z}{\sin\omega} = -\cot\omega\,.\,z + \frac{r}{r'}\frac{z'}{\sin\omega},$$

dus

$$\bar t'^{*} = (\cot\bar\omega - \cot\omega)\,.\,z + \frac{r}{r'}\,.\,\frac{z'}{\sin\omega} = \frac{\sin(\omega - \bar\omega)}{\sin\omega\,.\,\sin\bar\omega}\,.\,z + \frac{r}{r'}\,.\,\frac{z'}{\sin\omega}.$$

De eerste methode (*a*) heeft het voordeel, dat men werkt met de veranderlijken z en z', die veel zuiverder bepaald zijn dan de grootheden ζ en ζ'. Immers, om $\zeta_{k,l}$ en $\zeta'_{k,l}$ te bepalen, heeft men moeten interpoleeren tusschen de waarden $\zeta_{k-1/_2,l}$, resp. $\zeta'_{k,l-1/_2}$. Bovendien zijn deze laatste op zichzelf onzekerder dan de veranderlijken z en z', omdat ze uit kleinere frequentiesommen zijn berekend.

Het, overigens niet zeer belangrijke, nadeel van deze methode is, dat men bij het terugrekenen van de frequenties, hetzij uit (z, ζ^*), hetzij uit (z', ζ'^*), in geen van beide gevallen de gegeven frequenties precies terugkrijgt. Men kan echter de aldus berekende frequenties opvatten als vereffende empirische frequenties.

De tweede methode (*b*) heeft het voordeel, dat men bij het terugrekenen van de frequenties uit (z, ζ) de gegeven frequenties precies terugkrijgt. Daartegenover staat het nadeel, dat men, door zich uitsluitend naar het éène verdeelingsprincipe (z, ζ) te richten, de frequentieverdeeling hoogst eenzijdig behandelt, en dat men met name de betrekkelijk nauwkeurige grootheden z' bijna geheel veronachtzaamt.

Intusschen moet de praktijk in elk geval uitmaken, welke der beide vereffeningsmethoden de voorkeur verdient.

SKEW CORRELATION BETWEEN TWO VARIABLES.

Summary.

The aim of this paper is: to complete the results obtained in our former paper "On Treating Skew Correlation", [Proceed. of the K. Ak. v. Wet. Amsterdam, Vol. **38**, p. 797 and p. 919, Vol. **39**, p. 580 (referred to by S. C. *a*, *b*, *c*)], and to amend the conclusion enunciated S. C. *c*, p. 581, also making the footnote (p. 581) superfluous.

Instead of adjusting the points $P(z, \zeta)$ and $P'(z', \zeta')$ to the point P^*, situated on OPP', so that $OP^{*2} = OP \times OP'$ ($R^2 = r\,r'$, cf. (47), S. C. *c*, p. 581), we can better adjust P and P' in such a way *that one of the two unimodular variables* t *and* t' *becomes a function of only one of the primary variables* x *and* x'.

In order to construct $t(x)$, $t'(x, x')$, it is necessary:

1⁰. to introduce a constant angle $\overline{\omega}$,

2⁰. to leave the function $z(x)$ unaltered.

Among the innumerable methods, by which we can construct $t(x)$, $t'(x, x')$, we recommend especially the following two:

a. We keep z and z'. Then the points P and P' are shifted to a point P^* for which $z^* = z$, $z'^* = z'$ (fig. 4); thus ζ is changed into
$$\zeta^* = \frac{z' - \cos\omega \,.\, z}{\sin\omega} = -\cot\omega \,.\, z + \frac{z'}{\sin\omega}.$$

The angle ω is still taken from $\operatorname{tg}\omega = \frac{B}{A} = \frac{z\zeta' + z'\zeta}{zz' - \zeta\zeta'}$ (cf. (32), S.C. *b*, p. 928). Introducing the constant angle $\overline{\omega}$ (mean of the variable ω), *we*

obtain the same unimodular functions that we arrived at in the case $P' = P$ $(r' = r)$ (cf. (42), S.C. *b*, p. 935).

b. We keep z and ζ, or: we adjust P' to P (fig. 5). Here the unadjusted values z', ζ' serve only to determine ω (in cooperation with z, ζ). z' is afterwards adjusted to $z'^{*} = \frac{r}{r'} \,.\, z'$, becoming in this way a mixed function of x and x'. Introducing the constant $\bar{\omega}$, we obtain at last:

$$\bar{t} = \frac{z}{\sin \bar{\omega}} \quad , \quad \bar{t}'^{*} = \frac{\sin(\omega - \bar{\omega})}{\sin \omega \,.\, \sin \bar{\omega}} \,.\, z + \frac{r}{r'} \,.\, \frac{z'}{\sin \omega} \,.$$

As to (*a*): Advantage: we operate with z and z', which are determined more accurately than ζ and ζ' (these latter being computed from small frequencies, and affected by the incertainties of interpolation).

Drawback: By computung back the frequencies from (z, ζ^{*}) [or from (z', ζ'^{*})] we do not exactly get back the given frequencies.

As to (*b*): Advantage: By computing back the frequencies from (z, ζ) we obtain precisely the given frequencies.

Drawback: The frequency distribution is treated very partially, the comparatively accurate quantities z' being almost wholly neglected.

Hydrodynamics. — *On the application of statistical mechanics to the theory of turbulent fluid motion.* I. By J. M. BURGERS. (Mededeeling N⁰. 12 uit het laboratorium voor Aero- en Hydrodynamica der Technische Hoogeschool te Delft). (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of April 27, 1929).

1. *Introductory remarks.*

The study of the properties of the turbulent flow of a fluid through a cylindrical tube or between parallel walls forms one of the most interesting problems of hydrodynamics. The opinion has been expressed by various authors that this problem has to be attacked by the use of statistical methods. ¹) When compared with the classical problem of the kinetic theory of gases, however, the hydrodynamical case presents the difficulty that the system is not a conservative one: energy is continually being dissipated in consequence of the viscosity of the fluid, so that work has to be supplied from without in order that the mean flow may present a stationary character. A second difficulty is that it is not immediately clear what elementary processes or types of motion can be used as "objects" to be counted in order to arrive at a definition of the probability of a given type of flow.

In this paper an attempt is made to investigate somewhat more closely a way which perhaps might be followed in attacking this problem. In order to overcome the second difficulty we have restricted ourselves to the consideration of the two-dimensional case, so that the stream function ψ could be used as a basis for the description of the motion. Before starting with the formation of the equations, however, some general considerations shall be put forward, which resume what may be accepted about the character of turbulent flow, and partly go back to conclusions, stated already in 1895 by REYNOLDS. ²) They will bring us at the same time to some remarks about the first mentioned difficulty.

We remember that in studying the turbulent motion of a fluid in a tube or between parallel walls, it is customary to decompose the real motion in the so called *mean flow*, and the continually fluctuating *relative motion*. In the most important case, to which we shall restrict ourselves,

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¹) Comp. f.i. TH. VON KARMAN, Zeitschr. f. ang. Math. u. Mech. **1**, p. 250, 1921; Proc. Ist. Intern. Congress for Appl. Mech., Delft, 1924, p. 105; R. VON MISES, Zeitschr. f. ang. Math. u. Mech. **1**, p. 428, 1921; also a paper by the present writer in these Proc. **26**, p. 582, 1923.

²) O. REYNOLDS, Scientific Papers II, p. 535.

the mean flow is independent of the time. It appears from the equations deduced by REYNOLDS and by LORENTZ that the mean flow is influenced by the relative motion, as in the equations governing the former occur the mean values of the squares and the products of the velocity components of the relative motion. [1]) The principal object of the theory of turbulent flow is the calculation of these mean values, which in the case considered of a stationary mean motion, are independent of the time.

It is not impossible that the relative motion may be resolved into a "spectrum" of more or less regular periodical motions, "principal vibrations", the amplitudes and phases of which are continually changing. Each of these vibrations might perhaps be characterized by a certain dimension, a kind of "wave-length", the diameter of vortices belonging to it, or some suchlike quantity, and the spectrum might consist of vibrations of all kinds of wave-lengths, from great ones to small ones. The maximum wave-length will depend on the diameter of the tube, or the distance of the walls; on the other hand the minimum wave-length will be determined by the circumstance that vibrations of too small wave-length are damped out too fast by the internal friction of the fluid. It is to be expected that the ratio of the smallest wave-length to the diameter of the tube or the channel will be a function of REYNOLDS' characteristic number for the flow (product of mean velocity and diameter of tube or distance of walls, divided by the kinematical viscosity), and will be smaller, as this number becomes greater. On the other hand, when the REYNOLDS' number is so low, that the "smallest" wave-length should become greater than the maximum wave-length, relative motion is not possible at all, and the flow becomes regular or, as it is called, laminar.

In special cases, for instance when the walls of the tube or of the channel present rugosities of a definite period, it might be expected that certain vibrations in the spectrum will be much more prominent than the others. However, in the case of smooth walls, to which we shall adhere in the following lines, the mean amplitude probably will change rather gradually over the whole spectrum, and will depend on the REYNOLDS' number R only, in some analogous way as the energy distribution of black radiation depends on the absolute temperature.

It is of some use to introduce a "mean wave-length" λ_m of the relative motion. The ratio λ_m/l, where l is the cross dimension of the flow, will be a function of R, decreasing indefinitely as R increases. The quotient λ_m/V, V being the mean velocity of the fluid, may be taken as a measure for the "mean period" of the relative motion.

Returning now to the question of the dissipation of energy in the relative motion, we may point out that the amount of energy dissipated in the time λ_m/V is very small compared to the amount of energy present in this motion; the ratio of these amounts probably decreases again indefinitely as R increases. Hence there is some probability that in a first approximation we may treat the relative motion as if it was the motion of an ideal fluid and constituted a conservative system, and so the application of statistical mechanics to it might not be wholly unjustified. However, in the place of a given value of the total energy (which condition otherwise is of prime importance in statistical mechanics), we shall have to take the so-called *dissipation-condition*, which expresses that the relative motion obtains every second just as much energy from the mean motion, as it looses in the same time in consequence of the friction.

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[1]) O. REYNOLDS, l.c.; H. A. LORENTZ, Abhandl. über theoret. Physik, I, p. 43.

2. *Description of the field of flow; the probability hypothesis.*

We consider the two-dimensional flow which presents itself between two walls, placed at the distance l of each other, when one of them has a translational motion in its own plane with the velocity V with respect to the other. The REYNOLDS' number for the flow is: $R = \varrho\, Vl/\mu$ (ϱ: density, μ: ordinary viscosity); the frictional force on the walls will be called S. We use nondimensional variables by dividing all lengths by l, all velocities by V, etc.; moreover we put $C = S/\varrho V^2$. Denoting then the velocity of the mean flow by U (which is a function of y, increasing from 0 for $y = 0$ to 1 for $y = 1$), the instantaneous values of the velocity components of the relative motion by u, v, and using a bar to indicate mean values, we have as the equation for the mean motion: 1)

$$\frac{1}{R}\frac{dU}{dy} = C + \overline{uv} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The dissipation condition has the form:

$$-\iint dx\,dy\,\overline{uv}\,\frac{dU}{dy} = \frac{1}{R}\iint dx\,dy\,\overline{\zeta^2} \quad . \; . \; . \; . \; . \quad (2)$$

Here ζ is the vorticity of the relative motion. The integration with respect to y has to be extended from $y = 0$ to $y = 1$; that with respect to x over a length L, great compared with the distance of the walls. 2)

In order to abbreviate our formulae, we shall write:

$$-uv = t,\; -\overline{uv} = \overline{t},\; \zeta^2 = z,\; \overline{\zeta^2} = \overline{z} \quad . \; . \; . \; . \; . \quad (3)$$

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1) Compare O. REYNOLDS and H. A. LORENTZ, l.l.c.c., and also J. M. BURGERS, these Proc. **26**, p. 585, 1923.

2) For some considerations it may be convenient to suppose the channel to be closed in itself (imagine f.i. the space between two concentric cylinders, one of which is rotating with respect to the other). Then L is the total length of the channel. In order to avoid difficulties which might arise from the action of centrifugal forces, we have to assume that the radius of curvature of the walls of the channel is very large compared to the cross section of the latter.

The quantity $\bar{t}$ appears to be a function of y. It is everywhere positive and is zero at the walls; in the greater part of the field its value differs very little from the constant C. By integration of (1) we get:

$$C = \int_0^1 dy\, \bar{t} + R^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which formula also may be written:

$$C = \frac{1}{L}\int_{x_0}^{x_0+L} dx \int_0^1 dy\, \bar{t} + R^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4^a)$$

From the results of experimental researches on turbulent motion we can deduce that C is great compared with R^{-1}.

By eliminating dU/dy and C from (1), (2) and (4^a) we get an equation in which only the components of the relative motion occur, and which will give us the form of the dissipation condition, to be used subsequently: [1])

$$F \equiv \iint dx\, dy\, (\bar{t})^2 - \frac{1}{L}\left(\iint dx\, dy\, \bar{t}\right)^2 - \frac{1}{R}\iint dx\, dy\, \bar{t} +$$

$$+ \frac{1}{R^2}\iint dx\, dy\, \bar{z} = 0 \quad . \quad . \quad (5)$$

We introduce the stream function ψ for the relative motion; with it u, v, ζ are connected by the formulae:

$$u = \frac{\partial \psi}{\partial y}, \quad v = -\frac{\partial \psi}{\partial x}, \quad \zeta = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} = -\Delta \psi \quad . \quad . \quad . \quad . \quad (6)$$

Now in order to come to a statistical treatment of our problem, we first begin by reducing the field of the continuous variables x, y to a *discontinuous* field. We introduce a quadratic point lattice, with spacing ε, about which we suppose for the present that it is very small even compared to the "minimum wave-length" of the relative motion. The points will be distinguished by the indices k_1 (for columns, parallel to the y-axis) and k_2 (for rows, parallel to the x-axis); to simplify the formulae we combine these indices into the complex number $k = k_1 + ik_2$. Thus for instance, $k + i$ denotes the point just above the point k, $k-1$ the point just to the left, and so on. The total number of points, contained within the length L, will be denoted by N.

We now consider only the N values ψ_k which the function ψ takes at a given instant in the points of the lattice. In connection with this the formulae (6) will be replaced by the following ones:

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[1]) Comp. J. M. BURGERS, l.c., equation (14).

$$\left.\begin{aligned} u_k = \frac{1}{2\varepsilon}(\psi_{k+i} - \psi_{k-i}), \quad v_k = -\frac{1}{2\varepsilon}(\psi_{k+1} - \psi_{k-1}) \\ \zeta_k = \frac{1}{\varepsilon^2}(4\,\psi_k - \psi_{k+1} - \psi_{k+i} - \psi_{k-1} - \psi_{k-i}) \end{aligned}\right\} \quad . \quad . \quad (7)$$

Then we introduce an N-dimensional space with coordinates $\xi_1 \dots \xi_N$ and consider the point $\xi_1 = \psi_1$, $\xi_2 = \psi_2, \dots \xi_N = \psi_N$. This point gives us a representation of the state of the relative motion at the instant choosen. When in course of time the relative motion changes, the point will move through the ξ-space. We may imagine the various states of the relative motion at a series of instants with equal intervals of time between them to be represented simultaneously by a number of points, say M, in the ξ-space. These points will be crowded in those parts of the ξ-space, which represent states of the field occurring rather often, whereas their density will be less at parts, representing fields of less frequent occurrence. It is clear that when M is sufficiently great, mean values with respect to time of quantities depending on the ψ's of the relative motion, can equally well be calculated by using the points distributed over the ξ-space.

In order to formulate this more clearly, we divide the ξ-space into N-dimensional cells of volume $d\Omega$, the dimensions of which are small with respect to the values of ξ or ψ that have to be taken account of, but which at the other hand still each contain many points (this can be obtained by increasing M sufficiently). The numbers of points in those cells will be denoted by $n_1, n_2, n_3, \dots$; we put:

$$n = \nu M = f M \, d\Omega \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

so that:

$$\Sigma \, \nu = 1, \text{ or: } \int f \, d\Omega = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

(we may, according to circumstances, write either a summation or an integration). When now X is a function of the ψ_k (or ξ_k), the mean value of X can be found from:

$$\overline{X} = \Sigma \, \nu X = \int f X \, d\Omega \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

We now presume that the distribution of the points over the cells, i.e. the quantities ν or the function f, may be calculated as a most probable distribution, when account is taken only of some general conditions, viz. that u and v are zero at the walls, and that equation (5) is satisfied.

The conditions $u = v = 0$ at the walls become, when expressed by means of the stream function: $\psi = \partial\psi/\partial y = 0$ (that ψ has to take the *same* constant value at both walls is necessary in order that the relative motion shall present no mean flow). We shall translate these conditions by assuming that ψ has the value zero both at the wall and in the first row of points which extends along the wall; in the ξ-space this amounts to saying that a certain number of coordinates permanently has the value zero.

The dissipation condition can be translated as follows: from (7) we get, expressing the ψ's by the ξ's:

$$t_k = \frac{1}{4\varepsilon^2}(\xi_{k+1} - \xi_{k-1})(\xi_{k+l} - \xi_{k-l}) \quad \ldots \ldots \quad (11^a)$$

$$z_k = \frac{1}{\varepsilon^4}(4\,\xi_k - \xi_{k+1} - \xi_{k+l} - \xi_{k-1} - \xi_{k-l})^2 \quad \ldots \ldots \quad (11^b)$$

then from (10):

$$\bar{t}_k = \sum_{\xi} \nu\, t_k, \qquad \bar{z}_k = \sum_{\xi} \nu\, z_k \quad \ldots \ldots \quad (12)$$

where $\sum\limits_{\xi}$ is written to denote the summation over all elements of the ξ-space.

Substitution of these values into (5) gives us:

$$\varepsilon^{-2}\, F \equiv \sum_k \Big(\sum_{\xi} \nu\, t_k\Big)^2 - \frac{\varepsilon^2}{L}\Big(\sum_k \sum_{\xi} \nu\, t_k\Big)^2 - \frac{1}{R}\sum_k \sum_{\xi} \nu\, t_k + \frac{1}{R^2}\sum_k \sum_{\xi} \nu\, z_k = 0. \quad (13)$$

The summation $\sum\limits_k$ has to be extended over all points of the field between $y = 0$ and $y = 1$, $x = x_0$ and $x = x_0 + L$.

It is clear that this equation represents a relation between the ν's.

Finally, to obtain an expression for the statistical probability of a distribution of points over the ξ-space, we follow the lines, accepted in the kinetic theory of gases, and remark that there may be effected $M!$ permutations within the set of M points, all corresponding to one set ("ensemble") of fields of flow for the relative motion. When we do not count those permutations, in which only points belonging to one and the same cell change place (which would mean the permutation of fields of flow, differing only in a very slight degree), then there remain:

$$W = \frac{M!}{n_1!\, n_2!\, n_3! \ldots} \quad \ldots \ldots \quad (14)$$

permutations, in which points belonging to different cells are substituted for each other.

This formula remains indefinite as long as nothing has been said on the magnitude of the cells; therefore we shall assume that all cells have the same volume ω.

The quantity W thus obtained will be accepted as representing the *statistical probability* of the "ensemble" of fields of flow considered, and we can now put forward the hypothesis that an appropriate "ensemble", or in other words an appropriate set of points in the ξ-space, enabling us to calculate mean values by the aid of formula (10), will be obtained by taking the set, which, satisfying (13) and the condition that certain coordinates are permanently zero, makes W a *maximum*.

Before starting with the determination of this "most probable" set, the following remark must be made. When we consider the M fields of flow of the relative motion, which are represented by the M points in the ξ-space, then we must keep in mind that in reality each of these fields changes in course of time. As has been mentioned already we may imagine these changes to be pictured by a motion of the M points. Now in the case considered in the kinetic theory of gases great weight is attached to the circumstance that the representative points move in such a way that the density (per unit volume) of any cluster of points remains constant. This is known as LIOUVILLE's theorem, and is deduced from the canonical equations of motion.[1] It forms the basis for making the volume of all cells equal, as then a group of points, filling one cell, and hence representing fields of flow to be considered as indistinguishable from each other, always retains this property.

Now the question might be put forward if our set of points possesses the same property. At first sight this seems wholly improbable, as we have to do with a system that is essentially dissipative, and it is known that for a dissipative system, when left to itself, the property does not hold.[2] In the case of the turbulent flow, however, the state of things in some respects is a different one, as the dissipation of energy in the relative motion is balanced by the transference of energy to it from the mean motion. As the mechanism of this transference of energy is rather intricate, we may view the problem from another side by directing our attention to the real motion of the fluid, without introducing the distinction between mean flow and relative motion. If the stream function of the real motion is denoted by Ψ, we have the relations (t denoting for a moment the time):

$$\Psi = \psi + \int_0^{y} U\,dy, \qquad \frac{\partial \Psi}{\partial t} = \frac{\partial \psi}{\partial t} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and we may imagine the values of Ψ to be represented in the ξ-space, instead of those of ψ (the boundary conditions now change as Ψ is not zero for $y = 1$). When at the same time we consider a closed channel between two concentric cylinders of very great radius, in the way as has been indicated in footnote 2), p. 416, we have to do with a finite system, and now there is a balance between the energy dissipated in it and the work CL done in unit time by the forces that keep the walls in motion relatively to each other.

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[1] Comp. f.i. J. H. JEANS, The dynamical theory of gases (Cambridge 1916), p. 73.

[2] J. H. JEANS, l.c. p. 72.

There seem to be very few researches relating to the statistics of dissipative systems, kept in motion by the action of external forces. Mention may be made of an investigation by TREFFTZ on the behaviour of a dissipative system acted upon by a periodic force, in which case it can be proved that every stable motion of the system asymptotically becomes periodic with the same period as that of the force. [1]) Hence if in this case the states of an "ensemble" of such systems again are represented by a set of points, moving in some generalised space, they will not ultimately converge into some special points of this space, as it is the case with a dissipative system left to itself.

In the case of the turbulent motion of a fluid it seems allowable to suppose that the series of fields, evolving in course of time from any one, arbitrarily choosen as a starting point (perhaps with the exception of a multiplicity of less than N dimensions of singular points), will show the normal character of turbulent motion, assumed of course — as we tacitly have done in all considerations of this paper —, that the REYNOLDS' number of the flow lies sufficiently above its critical value. Hence the paths of the representative points in the ξ-space will not condense into special points, but will show some kind of cyclic character.

I have not been able to penetrate further into this matter, and in the consideration of this problem it is well necessary to keep in mind that the substitution of the point lattice for the real continuous field of motion, which substitution enables us to use the N-dimensional ξ-space, introduces an artificial element in our reasoning, i.e. the magnitude of the spacing ε between adjacent points. The following argument can perhaps make clear what is the meaning of this element: LIOUVILLE's theorem would be true for the set of points in the ξ-space, if the following equation could be proved:

$$\sum_k \frac{\partial \dot{\xi}_k}{\partial \xi_k} = 0 \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

where $\dot{\xi}_k$ represents the component along the ξ_k-axis of the velocity of a point in the ξ-space, considered as a function of its position, while the summation has to be extended over all coordinates of that point. Translating this into hydrodynamical terms: $\dot{\xi}_k$ denotes the value of $\partial \Psi / \partial t$ at a given point of the lattice in the field of flow, whereas the differentiation according to ξ_k means that we have to compare this value of $\partial \Psi / \partial t$ with that existing at the same point, when in this point (and in this point only) the stream function has been increased by a certain amount. In trying to effectuate this comparison with the aid of the hydrodynamical equations, we immediately see that in a continuous field the question has no meaning unless it be specified what is the extent of the area over which Ψ has to be increased.

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[1]) E. TREFFTZ, Zu den Grundlagen der Schwingungstheorie, Mathem. Ann. **95**, p. 307, 1925.

Whether this difficulty is a real or only an apparent one, I cannot say.¹) One other point may be mentioned, however. When in connection with the idea expressed at the end of § 1, we for a moment *neglect the viscosity*, and consider the motion of an ideal fluid between absolutely smooth walls, uninfluenced by external forces, then it seems that formula (16) will hold. A demonstration, though it is not an exact one, might be framed as follows: Using u, v, ζ now to denote quantities relating to the real motion, we have the relations:

$$\triangle \Psi = -\zeta, \quad \frac{\partial \zeta}{\partial t} = -u \frac{\partial \zeta}{\partial x} - v \frac{\partial \zeta}{\partial y} \quad \ldots \ldots \quad (17)$$

Let G be GREEN's function for the space between the walls; then we may express Ψ by the integral (c being a constant):

$$\Psi = cy + \iint G(x, y; x', y') \,.\, \zeta(x', y')\, dx'\, dy',$$

from which follows:

$$\frac{\partial \Psi}{\partial t} = \iint G(x, y; x', y') \,.\, \frac{\partial \zeta}{\partial t}\, dx'\, dy' \quad \ldots \ldots \quad (18)$$

We translate this integral into a summation over the points of the lattice, and at the same time express all quantities occurring in (17) by difference formulae of the type of equations (7). The function G changes into a set of numbers g_{kl}; in this case g_{kk} is finite. In this way (18) changes into:

$$\dot{\xi}_k = \frac{\partial \Psi}{\partial t} = \frac{1}{\varepsilon^2} \Sigma\, g_{kl}\, Z_l\, (\xi)$$

where Z_l is a quadratic function of the values of the ξ's at a certain group of points, situated around the point l. Every term occurring in Z consists of the product of two linear factors, each containing only *differences* of the values of ξ's. Hence in calculating the derivative with respect to ξ_k we shall get only terms containing such differences in the first degree. Now in making up the sum $\Sigma\, \partial \dot{\xi}_k / \partial \xi_k$ over all values of k,

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¹) As might be inferred from the circumstance that the REYNOLDS' number must be sufficiently high, the question will be connected with the problem of the stability of the turbulent motion, which has been considered by various authors (comp. f.i. F. NOETHER, Zeitschr. f. ang. Math. u. Mech. **1**, p. 125, 1921), and about which opinions still have not been settled. It has been supposed that the case of a fluid, moving between fixed walls under the action of a pressure gradient (or of gravity, when the flow is directed downwards), gives a better chance for a stable turbulent motion, than the case considered here. The formulae of § 2 can be extended to this case also; the principal change occurs in the dissipation condition.

it seems to be possible on account of the fact that we consider a closed channel, making use further of the properties

$$g_{k,\,k-1} = g_{k,\,k+1},\ \ g_{k,\,k-1+i} = g_{k,\,k+1+i},\ \text{etc.},$$

to prove that all terms cancel.[1])

In the case of an ideal fluid this property may be accepted as a justification for taking the stream function as a basis for the determination of the probability, without trying to seek for a kind of canonical variables, and for assuming that the volumes of all cells in the ξ-space must be equal.[2]) In doing the same thing for the case of a viscous fluid, it is possible of course that we assign too great a probability to states of motion which are damped so soon by the viscosity that they practically speaking never occur; however, as the dissipation condition already prevents a frequent occurrence of such states, we may preserve the hope that calculations based on this assumption will not be altogether useless.

3. *Calculation of the most probable distribution.*

By the application of STIRLING's formula we get the well known approximation for the logarithm of (14):

$$lg\, W \cong -\Sigma\, n\, lg \frac{n}{M} = -M\, \Sigma\, \nu\, lg\, \nu\, . \quad . \quad . \quad . \quad . \qquad (19)$$

The quantities ν have to satisfy the equations (9) and (13). An arbitrary variation of one of the ν's with the amount $\delta\nu$ produces in (9) the variation:

$$\delta\, \nu \,.\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ .\ \ . \qquad (a)$$

and in (13):

$$\varepsilon^{-2}\, \delta F = \left\{ 2 \sum_k \left(t_k \sum_{\xi'} \nu\, t_k(\xi') \right) - \frac{2\varepsilon^2}{L} \left(\sum_k t_k \right) \left(\sum_{k'} \sum_{\xi'} \nu\, t_{k'}(\xi') \right) - \right.$$
$$\left. - \frac{1}{R} \sum_k t_k + \frac{1}{R^2} \sum_k z_k \right\} \delta\nu$$

for which, using the abbreviation:

$$\frac{2\varepsilon^2}{L} \sum_{k'} \sum_{\xi'} \nu\, t_{k'}(\xi') - 2 \sum_{\xi'} \nu\, t_k(\xi') + R^{-1} = \varphi_k \quad . \quad . \quad . \quad . \qquad (20)$$

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[1]) Another deduction will be given in Part II. (Note added in the proof).

[2]) The question whether it is possible to make use of canonical variables, however, still deserves attention, though it seems that the stream function at any rate leads to more simple formulae. In the case of the motion in an ideal fluid of parallel rectilinear vortices, the diameters of which are very small compared to their distances, canonical variables can be introduced according to a method developed by KIRCHHOFF and by LAGALLY (comp. M. LAGALLY, Sitz. Ber. Münch. Akad. p. 377, 1914). For these coordinates LIOUVILLE's theorem can be proved. In applying statistical methods now the kinetic energy of the motion has to be given.

we may write:

$$\varepsilon^{-2}\,\delta F = \left\{ \sum_k \left(\frac{z_k}{R^2} - \varphi_k\, t_k \right) \right\} \delta\nu \quad . \; . \; . \; . \; . \; . \; . \qquad (b)$$

Finally the variation of $lg\,W$ becomes:

$$\delta\, lg\, W = -M\,(lg\,\nu - 1)\,\delta\nu \quad . \; . \; . \; . \; . \; . \; . \qquad (c)$$

In order to arrive at the solution of the maximum problem we have to assume that a linear relation exists between the coefficients of $\delta\nu$ in the expressions (*a*), (*b*), (*c*); hence we get:

$$lg\,\nu = \alpha - \beta \sum_k \left(\frac{z_k}{R^2} - \varphi_k\, t_k \right)$$

or:

$$\nu = A\, e^{-\beta \sum\limits_k \left(\frac{z_k}{R^2} - \varphi_k\, t_k \right)} \quad . \; . \; . \; . \; . \; . \; . \qquad (21)$$

The quantities α (resp. A) and β are constants, the values of which have to be determined by substituting the expression (21) in the equations (9) and (13). $\Sigma\nu$ will not be convergent unless we suppose $\beta > 0$; whether this condition suffices to ensure the convergence in all circumstances has to be investigated afterwards. Provisionally we will accept that no difficulties are concealed behind this question.[1]

The expression (21) in reality is an implicit equation for the ν's, as the quantities φ_k, occurring in the exponent, are a function of them.

It is of importance to consider φ_k in more detail. According to (12) and to (4) or (4*a*) we may write:

$$\sum_{\xi'} \nu\, t_k\,(\xi') = \bar{t}_k\,; \quad \frac{2\,\varepsilon^2}{L} \sum_{k'} \sum_{\xi'} \nu\, t_{k'}\,(\xi') = \frac{2\,\varepsilon^2}{L} \sum_{k'} \bar{t}_{k'} = 2 \int_0^1 dy\, \bar{t} = 2\,(C - R^{-1});$$

by means of this we get:

$$\varphi_k = 2\,C - R^{-1} - 2\,\bar{t}_k \quad . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (22)$$

In the vicinity of the walls $\bar{t}$ becomes zero; hence φ will be positive here, so that fields of flow, possessing positive values of t in the neighbourhood of the walls, will be much more frequent than their images with respect to x- or y-axis, with negative values of t.

In the more central part of the field on the contrary, $\bar{t}$ is only slightly smaller than C, so that φ becomes small here. It is probable that φ still will be positive, as otherwise fields with negative values of t in this region would be more occurrent than such with positive values, which is impossible as the mean value $\bar{t}$ ought to be positive. If we accept this supposition, we must conclude that $\bar{t} < C - \frac{1}{2} R^{-1}$.[1]

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[1] A further investigation of this point leads to a condition for the function φ, as will be shown in Part II. (Note added in the proof).

Another expression for φ may be found by eliminating $\bar{t}$ with the aid of (1); in this way we shall get:

$$\varphi = \frac{1}{R}\left(2\,\frac{dU}{dy} - 1\right) \quad \ldots\ldots\ldots \quad (23)$$

When now we calculate $\bar{t}$ by means of (12) and (21), we arrive at the following equation:

$$\bar{t}_k = A \sum_{\xi} t_k(\xi)\, e^{-\beta \sum_{l} \left\{ \frac{z_l(\xi)}{R^2} - \left(2\,C - R^{-1} - \bar{t}_l(\xi)\right) \right\}} \quad . \quad . \quad (24)$$

Here $t_k(\xi)$, $z_l(\xi)$, $t_l(\xi)$ represent known functions of the ξ's; the first summation is extended over the ξ-space, the second one over the points of our lattice in the field of flow.

The equation represents an integral equation for $\bar{t}$; it is of importance in the investigation of the resulting field of flow as by the use of (1) and (4) we can calculate the distribution of the velocity and the resistance coefficient as soon as $\bar{t}$ is known.

We hope to come back to a discussion of some of the suppositions made in this paper in a further communication.

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[1] It might be supposed that even when φ is negative in the central region, fields with positive values of t may be supported by their parts lying in the region along the walls. This would demand, however, for a coherence in these fields extending over rather great distances, which seems improbable.

As we may conclude from (4) that in the central part of the field $\bar{t}$ must be greater than $C - R^{-1}$, we see that $\bar{t}$ here is enclosed between rather narrow limits.

Biochemistry. — *The conditions of activation of washed zymin in relation to the co-enzyme problem.* By A. A. STHEEMAN. (Communicated by Prof. A. J. KLUYVER.)

(Communicated at the meeting of April 27, 1929).

I.

Until lately our knowledge of the co-enzyme of alcoholic fermentation was practically restrained to the fact that it is an ultrafiltrable, dialysable, thermostable principle. By special procedures the usual zymase preparations can be treated in such a way that they lose their power to ferment the hexoses to alcohol and carbon dioxide even in the presence of alkaliphosphates. The zymase considered from the point of view of its function to split hexoses has become inactivated. This inactive zymase is reactivated when besides the due amount of alkaliphosphate a co-enzyme containing solution is added.

In 1927 KLUYVER and STRUYK [1]) submitted the co-enzyme to a closer investigation; their results throw fresh light on the nature and the meaning of the co-enzyme and allow of the explanation of many uptill now unaccountable facts.

KLUYVER and STRUYK in their experiments made use of maceration juice which, by washing on an ultrafilter, was deprived of its property to ferment glucose in the presence of alkaliphosphates. The zymase thus rendered inactive could be reactivated not only by adding to it a co-enzyme containing solution but also by the addition of various substances. Which of these substances were capable of reactivation of the inactivated zymase appeared to depend on the extent in which the zymase was washed, thus on the degree of dilution of the admixtures occurring next to the zymase in the original maceration juice. As substances which according to circumstances, suffice alone or together to reactivate the inactivated zymase KLUYVER and STRUYK mention acetaldehyde, hexosebiphosphate and anti-autolytic principles.

It could now be shown by KLUYVER and STRUYK that an inactivation of the zymase (to such an extent that by addition of co-enzyme reactivation of the zymase could take place) was the result of the elimination of one or more of the three substances mentioned above, from the original zymase preparation.

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1) A. J. KLUYVER and A. P. STRUYK, These Proc. Vol. **30**, 569 (1927).
A. J. KLUYVER and A. P. STRUYK, Biochem. Z. **201**, 212 (1928).
A. P. STRUYK, Dissert. Delft, 1928.

They supported their view a.o. by experiments with a maceration juice which had been washed to such an extent as to be, according to MEYERHOF, free from co-enzyme. They shomed that a maceration juice treated in such a way would no longer ferment glucose even after the addition of hexosebiphosphate and they were able to reactivate this "maceration juice free from co-enzyme" by adding to it besides hexosephosphate, the "Schutzsaft" made according to HAEHN and SCHIFFERDECKER [1]).

As HAEHN and SCHIFFERDECKER established the antiproteolytic action of this "Schutzsaft" KLUYVER and STRUYK could make it acceptable that in the above case a co-enzyme like action might be obtained by the addition of hexosebiphosphate and antiproteolytic substances to the apo-zymase. At the same time KLUYVER and STRUYK demonstrated that the "Schutzsaft" could be substituted by an aqueous extract of a co-enzyme free maceration juice.

From their experiments KLUYVER and STRUYK conclude that the conception of the indispensability of a "co-enzyme" in "cellfree" alcoholic fermentation must give place to the view that a normal fermentation of hexoses by means of zymase cannot proceed unless some conditions have been fulfilled viz. that besides alkaliphosphates, an initiating hydrogen acceptor, hexosebiphosphate and antiproteolytic substances must occur in the fermentation mixture.

Now it seemed of importance to investigate in how far the results got by KLUYVER and STRUYK in their work with maceration juice could also be obtained if instead of maceration juice zymin was used.

Experimental.

II.

The zymin used in the experiments was obtained from a Dutch baker yeast (named "koningsgist") from the "Nederlandsche Gist- en Spiritusfabriek" at Delft. It was prepared by the usual method of treatment with acetone and ether [2]). From 500 grams of yeast ca. 125—130 grams of a very fine yellow white powder are obtained. The washing of the zymin. to inactivate the zymase, was performed by vigorously shaking one part of the zymin with eight or ten parts of cold tap water in a small Erlenmeyer flask for two minutes. This done the flask was only gently shaken for a few seconds every three minutes to keep the zymin suspended in the water. After having been washed in this way for ten or fifteen minutes, the zymin suspension was centrifuged. The residue was suspended in water and washed again if necessary or made up to a given volume with distilled water. In each experiment 5 cc. of the zymin suspension were added to the solutions, the power of which had to be investigated of reactivating the inactive zymase, and the whole made up to 10.3 cc. Some toluene was added and thoroughly mixed with the zymin suspension. After the excess of toluene had come again to the surface one cc. of each mixture was introduced into a quantitative fermentation apparatus according to VAN ITERSON—KLUYVER [1]). A series of these apparatus was placed in a HEARSON incubator which was kept at a constant temperature of 25° C. The above apparatus has the advantage that fermentation is carried out under *strictly* anaerobical conditions and that moreover the volume of the carbon dioxide evolved can be read directly at atmospheric pressure. All solutions used in the experiments were previously saturated with carbon dioxide at the temperature of 25° C.

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[1]) H. HAEHN und H. SCHIFFERDECKER, Biochem. Z. 138, 209 (1923).

[2]) A. HARDEN, Alcoholic fermentation 3rd. Ed. 1923 p. 38.

The hexosebiphosphate solution used was obtained by decomposing the pure Ba-salt with cold diluted sulfuric acid and (after removal of the barium sulfate by centrifuging) by neutralizing the clear colourless solution of the acid with diluted sodium hydroxide until faintly pink to phenolphtaleine. Immediately after this the solution was saturated with carbon dioxide.

The methylenblue used was a saturated solution of the pure substance (free from zinc chloride) in distilled water.

The first washing of the zymin, after having been boiled, filtered and concentrated on the water-bath to one tenth of its original volume was used as "co-enzyme" solution. This concentration was chosen because in this way the total amount of inorganic *P* was equal to the amount used in the other experiments of the same series.

Numerous series of experiments were made ; some of these series which can easily be reproduced are mentioned below.

III.

A. This series of experiments shows that it is possible to reactivate a zymin inactivated by washing by means of the addition either of acetaldehyde or of methylenblue, or of hexosebiphosphate or of a "co-enzyme" containing solution.

10 grams of zymin were washed once with 10 parts of water for 15 minutes, centrifuged for another 15 minutes and made up to 75 cc. In each experiment 5 cc. of this suspension ($^2/_3$ gram of zymin) were added to the following solutions and made up with water to a total volume of 10.3 cc. One cc. of each of these mixtures was introduced into the fermentation apparatus.

The solutions contained :

Exp. 1. 2 cc. 0.5 M K_2HPO_4 + 0.5 gr. glucose

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[1]) C.f. A. J. KLUYVER, Dissert. Delft 1914.
A. W. VAN DER HAAR, Anleitung zum Nachweis der Monosaccharide und Aldehydsäuren. Berlin 1920.

Exp. 2. 2 cc. 0.5 M K_2HPO_4 + 1 cc. acetaldehyde (1 %) + 0.5 gr.
[glucose
Exp. 3. 2 cc. 0.5 M K_2HPO_4 + 2 cc. methylenblue + 0.5 gr. glucose
Exp. 4. 2 cc. 0.5 M K_2HPO_4 + 3 cc. Na-hexosebiphosph. + 0.5 gr.
Exp. 5. 2 cc. 0.5 M K_2HPO_4 + 1 cc. acetaldehyde (1 %) [glucose
Exp. 6. 1 cc. acetaldehyde (1 %) + 0.5 glucose
Exp. 7. 5 cc. boiled washing (conc.) + 0.5 gr. glucose
Exp. 8. 5 cc. boiled washing (conc.)
Exp. 9. 1 cc. 0.5 M K_2HPO_4 + 4 cc. boiled washing + 0.5 gr. glucose
Exp. 10. 1 cc. 0.5 M K_2HPO_4 + 4 cc. boiled washing + 0.5 gr. glucose
Exp. 11. 2 cc. 0.5 M K_2HPO_4 + 0.5 gr. fructose
Exp. 12. 2 cc. 0.5 M K_2HPO_4 + 1 cc. acetaldehyde (1 %) + 0.5 gr. fruct.
Exp. 13. 2 cc. 0.5 M K_2HPO_4 + 0.5 cc. methylenblue + 0.5 gr.
[glucose

The hexosebiphosphate solution used, contained 2 mgr. of combined phosphorus per cc.

TABLE A.

Time in hours:	Evolution of CO_2 in cc. at atmospheric pressure.												
	Number of experiment.												
	1	2	3	4	5	6	7	8	9	10	11	12	13
$1^1/_2$	—	1.7	0.8	1.5	—	—	2.8	1.0	2.5	1.6	—	0.2	—
3	—	2.9	2.3	3.1	—	—	4.0	1.3	4.6	3.2	—	2.2	—
5	—	3.8	3.4	4.3	—	—	5.3	1.5	6.4	4.0	—	3.2	—
18	—	10.3	10.8	10.8	0.05	—	12.2	1.9	12.0	10.9	—	9.0	—

The experiments which did not give any evolution of gas after 18 hours were still negative after 48 hours.

Exp. 1 shows that no evolution of gas occurs in the absence of acetaldehyd, whereas a nearly quantitative fermentation is produced in the presence of this substance (exp. 2) or of methylenblue (exp. 3) 1). From this it follows without any doubt that the activating effect of these two substances must be ascribed to their action as a hydrogen acceptor.

Exp. 5 and 6 prove that the washed zymin contained neither fermentable substances nor free phosphate; so the carbon dioxide evolved has its origin in the fermentation of the glucose which has been added. The washing used in exp. 10 was boiled for 7 hours at a refluxcondensor before

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1) To attain the same stage of inactivation with a zymin prepared from top-fermentation yeast from a Dutch brewery, three times washing for twenty minutes with six parts of water proved to be necessary.

it was concentrated; in this way the great thermostability of the "co-enzyme" was demonstrated.

Before discussing the activation produced by the addition of hexosebiphosphate, we must draw the attention to some properties of the boiled washing. In the first washing, after being boiled and filtered the still dissolved protein substances were removed by adding trichloracetic acid. In a part of the clear filtrate free phosphate and a substance behaving as a ketohexose (Seliwanoff-test) could easily be detected. To another part of the filtrate barium acetate in excess was now added and cold baryta until just pink to phenolphtaleine. After this the solution was heated to boiling and filtered rapidly, in the filtrate free phosphate could no more be detected and a positive Seliwanoff-test could no more be obtained. It is highly probable therefore that the positive Seliwanoff-test in the boiled washing must be ascribed to the presence of hexose biphosphate.

From this we may conclude that by the first washing the greater part of the hexosebiphosphate present in the zymin has been removed. The fact however that in the zymin used in the experiments mentioned above still some hexosebiphosphate is left can be proven by washing it a second time. With a part of this washing still a positive Seliwanoff-test can be obtained, though it is very faint.

Exp. 4 is showing that addition of hexosebiphosphate, removed by the washing, is sufficient to induce a normal fermentation. The hexosebiphosphate added here fulfils the function of a hydrogen acceptor (cf. exp. 3).

KLUYVER and STRUYK (l.c.) already observed the fact that this substance in not too small a concentration can act in this way. Besides this they consider it probable that hexosebiphosphate has still another function in the mechanism of alcoholic fermentation which is depending on the presence of the esterified phosphoric group.

We may now explain the activation observed in the experiments after the addition of a hydrogenaccepting substance or of hexosebiphosphate by assuming that there is still enough hexosebiphosphate left in the washed zymin for the second function, provided there is another hydrogenacceptor present which can replace the hexosebiphosphate removed.

Indeed exp. 14 in comparison with exp. 3 proves very clearly that a minimum amount of a hydrogen acceptor is required for the initiation of the fermentation viz. that activation is also dependent on the quantity of the hydrogenaccepting substance added.

The amount of hexosebiphosphate removed by the first washing being considerable was shown by an estimation of this substance which gave 20 milligrams of P. as hexosebiphosphate in the first washing of 10 grams of zymin.

B. The experiments show that the zymin after having been twice washed cannot be reactivated by acetaldehyde or methylenblue, whereas a nearly quantitative fermentation of the glucose occurs when hexosebiphosphate is added.

9 grams of zymin were washed one time with 8 parts of water for 10 minutes and centrifuged. The residue was suspended in 8 parts of water and shaken for two minutes. Immediately after this the suspension was centrifuged again and the residue was made up with water to 60 cc. In each experiment 5 cc. of this suspension (0.75 gram of zymin) was added to the solutions and made up to 10.3 cc. One cc. of each of these mixtures was introduced into the fermentation apparatus.

The solutions contained:

Exp. 1. 2 cc. 0.5 M K_2HPO_4 + 0.5 grams glucose
Exp. 2. 2 cc. 0.5 M K_2HPO_4 + 1 cc. acetaldehyde (1 %) + 0.5 gr. [glucose
Exp. 3. 2 cc. 0.5 M K_2HPO_4 + 2 cc. methylenblue + 0.5 gr. glucose
Exp. 4. 2 cc. 0.5 M K_2HPO_4 + 2 cc. Na-hexosebiphosph. + 0.5 glucose
Exp. 5. 2 cc. 0.5 M K_2HPO_4 + 2 cc. Na-hexosebiphosph. + 1 cc. acetaldehyde (1 %) + 0.5 gr. glucose
Exp. 6. 5 cc. boiled washing (conc.) + 0.5 gr. glucose
Exp. 7. 5 cc. boiled washing (conc.)
Exp. 8. 2 cc. 0.5 M K_2HPO_4 + 0.5 cc. Na-hexosebiphosphate + 0.5 gr. glucose
Exp. 9. 2 cc. 0.5 M K_2HPO_4 + 1 cc. acetaldehyde (1 %) + 0.5 gr. fructose
Exp. 10. 2 cc. 0.5 M K_2HPO_4 + 2 cc. Na-hexosebiphosphate + 1 cc. acetaldehyde (1 %) + 0.5 gr. fructose
Exp. 11. 2 cc. 0.5 M K_2HPO_4 + 2 cc. Na-hexosebiphosphate + 0.5 gr. fructose.

The hexosebiphosphate solution contained 2 mg. per cc.

TABLE B.

Time in hours:	Evolution of CO_2 in cc. at atmospheric pressure.										
	Number of experiment.										
	1	2	3	4	5	6	7	8	9	10	11
$1^1/_2$	—	—	—	0.4	0.2	2.1	0.8	—	—	—	-
3	—	—	—	1.9	1.2	3.2	1.0	—	—	—	0.1
5	—	—	—	3.5	3.0	5.0	1.5	—	—	0.1	0.8
20	—	—	—	10.3	9.4	11.9	2.0	—	—	0.2	1.6

The experiments which showed no evolution of gas remained negative even after 40 hours.

These experiments show that by the second short washing, the hexosebiphosphate content of the zymin was now lowered to such an amount that fermentation of the glucose was made impossible [1]). The addition of a sufficient amount of hexosebiphosphate is required for the reactivation of the zymase.

It is interesting that fructose which in the first series of experiments was fermented at the same rate as glucose in this series shows a different behaviour.

C. The following experiments show that when the washing of the zymin is performed more intensively the addition of hexosebiphosphate is no longer sufficient to activate the washed zymin. The addition of a solution containing an extract of a zymin "free from co-enzyme" to the fermenting mixture is necessary to enable the zymase to ferment the glucose at a normal rate.

9 grams of zymin were twice washed for 15 minutes with 10 parts of water. The zymin suspension was made up to 60 cc. In each experiment 5 cc. of this suspension (0.75 gram of zymin) was added to the solutions and the mixture made up with water to 10.3 cc. One cc. of each of these mixtures was introduced into the fermentation apparatus.

The hexosebiphosphate solution used contained 5 mg. organic P. per cc.

Besides 0.5 gram of glucose the solutions contained:

Exp. 1. 2 cc. 0.5 M K_2HPO_4
Exp. 2. 2 cc. 0.5 M K_2HPO_4 + 1 cc. acetaldehyde (1 %)
Exp. 3. 2 cc. 0.5 M K_2HPO_4 + 2 cc. methylenblue
Exp. 4. 2 cc. 0.5 M K_2HPO_4 + 1 cc. Na-hexosebiphosphate
Exp. 5. 2 cc. 0.5 M K_2HPO_4 + 1 cc. Na-hexosebiphosphate + 1 cc. acetaldehyde (1 %)
Exp. 6. 1 cc. 0.5 M K_2HPO_4 + 2 cc. proteinsolution f.f.c.
Exp. 7. 1 cc. 0.5 M K_2HPO_4 + 2 cc. proteinsol. f.f.c. + 1 cc. acetaldehyde (1 %)
Exp. 8. 1 cc. 0.5 M K_2HPO_4 + 3 cc. proteinsol. f.f.c.
Exp. 9. 1 cc. 0.5 M K_2HPO_4 + 1 cc. Na-hexosebiphosphate + 2 cc. proteinsol. f.f.c.
Exp. 10. 1 cc. 0.5 M K_2HPO_4 + 0.5 cc. Na-hexosebiphosphate + 2 cc. [proteinsol. f.f.c.
Exp. 11. 5 cc. boiled washing (concentrated).

The mode of preparation of the proteinsolution "free from co-enzyme" (f.f.c.) is given below.

As the figures show, in this series the washed zymin suspension can no longer be reactivated by the addition of an amount of hexosebiphosphate which corresponds to 50 mgr. of the Ba-salt. per 10.3 cc. According to the current view the zymin must be considered to be free from co-enzyme (MEYERHOF). The zymase is however reactivated (exp. 9) by the addition

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[1]) Zymin prepared from a top-fermentation yeast had to be washed three times for half an hour with six parts of water to obtain this stage of inactivation

TABLE C.

Time in hours:	Evolution of CO_2 in cc. at atmospheric pressure.										
	Number of experiment										
	1	2	3	4	5	6	7	8	9	10	11
2	—	—	—	—	—	—	—	—	—	—	3.8
4	—	—	—	—	—	—	—	—	0.7	0.1	6.6
6	—	—	—	—	—	—	—	—	2.5	0.4	9.5
20	—	—	—	—	—	—	—	—	10.4	0.6	13.2
48	—	—	—	—	—	—	—	—	11.6	0.5	13.0

of a proteinsolution made from a zymin "free from co-enzyme". From this it follows that the co-enzyme according to MEYERHOF is present in or can be prepared from a zymin which itself is free from this co-enzyme. These experiments show that the results obtained by KLUYVER and STRUYK, in their experiments with maceration juice, are substantiated by those with zymin.

As the zymase is also activated by the addition of the boiled washing we must conclude that, besides hexosebiphosphate this solution contains an active principle which is present in a zymin washed until it is free from co-enzyme.

The "proteinsolution free from co-enzyme" was obtained from a zymin which was rendered inactive by thrice washing it for ten minutes with eight parts of water. Experiments were carried out which proved that the zymin would not ferment glucose even after the addition of an amount of hexosebiphosphate which corresponds to 150 mg. of the Ba-salt per 10.3 cc. The washed zymin (from 9 grams of dry zymin) was made up with water to 30 cc. and placed at 35° C. for three to four hours, toluene being added. After this 6 cc. 0.5 K_2HPO_4 were added and the suspension was boiled for two minutes, then 30 cc. of water were added and the suspension gently boiled again for ten minutes. After cooling and centrifuging the residue was suspended in 50 cc. of water and boiled again. After having been centrifuged the centrifugate was added to the former. The clear pale yellow solution (ca. 100 cc.) which showed strong protein reactions was concentrated on the water-bath to 12 cc. One cc. of this concentrate thus corresponds to 0.75 gram of dry zymin and contains 0.5 cc. of 0.5 M K_2HPO_4.

D. When the washing of the zymin is continued a stage is reached in which the inactivated zymase will not ferment glucose even after the addition of hexosebiphosphate in large amounts and of the protein solution f.f.c., whilst the addition of the boiled washing still produces a quantitative fermentation.

9 grams of zymin were thrice washed for ten minutes with 8 parts of water and made up to 48 cc. 4 cc. of this suspension (0.75 gr. of zymin) were added to the following solutions and made up with water to a total volume of 10.3 cc. One cc. of each of these mixtures was introduced into the fermentation apparatus.

The hexosebiphosphate solution used contained 10 mg. organic P per cc.

Besides 0.5 gr. of glucose the solutions contained:

Exp. 1. 2 cc. 0.5 M K_2HPO_4 + 1 cc. acetaldehyde (1 %)
Exp. 2. 2 cc. 0.5 M K_2HPO_4 + 2 cc. methylenblue
Exp. 3. 2 cc. 0.5 M K_2HPO_4 + 0.75 cc. Na-hexosebiphosphate
Exp. 4. 2 cc. 0.5 M K_2HPO_4 + 1.5 cc. Na-hexosebiphosphate
Exp. 5. 2 cc. 0.5 M K_2HPO_4 + 3.0 cc. Na-hexosebiphosphate
Exp. 6. 3 cc. Na-hexosebiphosphate solution
Exp. 7. 0.5 cc. 0.5 M K_2HPO_4 + 3 cc. proteinsol. f.f.c.
Exp. 8. 0.5 cc. 0.5 M K_2HPO_4 + 3 cc. proteinsol. f.f.c. + 1.5 cc. Na-hexosebiphosphate
Exp. 9. 1.0 cc. 0.5 M K_2HPO_4 + 2 cc. proteinsol. f.f.c. + 1.5 cc. Na-hexosebiphosphate
Exp. 10. 1.0 cc. 0.5 M K_2HPO_4 + 2 cc. proteinsol. f.f.c. + 3.0 cc. [Na-hexosebiphosphate
Exp. 11. 5 cc. boiled washing conc.

Exp. 1—11 contained the same amount of anorganic phosphate as the boiled washing (resp. 31.2 and 31.0 mg. P). The quantity of hexosebiphosphate in the boiled washing was estimated and amounted to 12.2 mg. P. in the 5 cc. used.

Exp. 1 until and including exp. 10 did not show the slightest evolution of gas even after 48 hours.

Exp. 11 gave the following figures:

1½ hours 3.1 cc., 3 h. 4.2 cc., 5 h. 5.5 cc., 24 h. 12.4 cc., 48 h. 12.6 cc.

The same protein solution f.f.c. had been used in the experiments in C. and in those mentioned above. Still we see that the addition of the protein solution f.f.c. along with hexosebiphosphate does not longer suffice to restore the fermentative power of the washed zymin. We may therefore conclude that in the last mentioned series besides the two substances mentioned still another substance is indispensable to produce the same reactivating effect as is characteristic for the boiled washing.

We may summarize the result obtained here in this way: Probably to the three already known factors, indispensable for a normal cell-free fermentation, at least one more must be added.

E. When the zymin is washed with 8 parts of water once for 30 minutes and twice for 15 minutes the addition even of the boiled washing cannot reactivate any more the zymase; the enzyme is irreversibly inactivated.

Utrecht, April 1929.

Physics. — *The ultra violet radiation in tropical sunlight.* By J. C. BOEREMA and M. P. VRIJ. (Communicated by Prof. P. ZEEMAN.)

(Communicated at the meeting of April 27, 1929).

Since we know, what ultra violet radiation means for the life of men, animals and plants and which results the ultra violet radiation therapy attains, the investigations of the quantity and the extensiveness of the U. V. in sunlight is more than urgent.

However the radiation of the sun is till now measured at few places yet. This is undoubtedly due to difficulties which append to those measurements, when a rather high accuracy is aimed at. Thereby one has only few data yet about Europe and America and about the tropical zones one knows yet nothing at all[1]).

Besides the already mentioned practical use, the investigation of the U. V. in sunlight has also much scientific importance. The quantity of ozone in the upper layers of the atmosphere is connected directly with it and therewith again other phenomena in the upper layers of the atmosphere.

Moreover there prevails in the tropical lands a very fixed opinion notwithstanding the absolute missing of any data. It is remarkable, how universally and how positively the opinion is announced, that the tropical sunlight would have less U. V. than the sunlight in moderate zones. All those assertions however depend on no exact measurements at all. There is a wide spread opinion that it is allowed to draw upon this conclusion from the remarkable matter of fact, that photographing in the so brilliant, nearly shrill tropical light needs a positively longer time of exposure than in Europe or America.

Thus there are very many reasons to begin as soon as possible with the measurements in the ultra violet of tropical sunlight. Therefore the results of our preliminary investigations follow here.

With the aid of a little quartz spectrograph of Hilger (E 31) mounted on a foot with two perpendicular axes, the spectrum of the sun was photographed. The sunlight fell directly on the split of the spectrograph.

The great difference in intensity between the visible and the ultra violet part of the spectrum causes two difficulties for the spectroscopical exposures. In the first place the time of exposure can never been chosen in such a way, that it is as good as possible for the whole spectrum. The visible part is already long time overexposed, while the extreme U. V. is yet underexposed. More over a diffuse scattering occurs in the instrument on the bounding surfaces of lenses and prisma, by which especially in the U. V. an inconvenient fogging comes on.

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[1]) The measurements of P. C. FREER, Transact. second Biannial Congres Hongkong 1912, p. 186—214 do not satisfy the requirements, demanded nowadays by a scientific investigation of radiation and therefore they have no importance for us; at best they stimulate to further investigation.

We mean however that the results deduced from these first exposures are of sufficient importance to give already now a paper about them.

We express our sincere thanks to Prof. Dr. P. ZEEMAN in Amsterdam for his readiness for making in his laboratory photograms of a number of our exposures with a Moll photometer. From the photograms, got in this way can be deduced, that in Batavia in the months of August, September and October [1]) (1928) the spectrum of the sun extended to 2954 Å or further and this during at least four hours of the day. It never was observed that it normally ended before 2954 Å. Very often a limit yet lower could be found which means a yet further extension of the U. V.

From these preliminary exposures nothing can be concluded, we regret to say, about the true relations of intensities in the spectrum of the sun. We can however properly suppose, that a greater extension of the U. V. is coupled with a greater intensity of the U. V. The absorption of the U. V. part of the sunlight occurs namely according to the investigations of FABRY and BUISSON [2]), DOBSON [3]) a.o. principally by the ozon present in the upper layers of the atmosphere. The absorption increases continually with shorter wavelengths and thus a new region will only be noticed on earth, as soon as it is less absorbed by that layer of ozone. But then also the U. V. of longer wavelengths in less absorbed and this will be increased thus in intensity, as is shown by the following table, taken from the work of FABRY and BUISSON [4]). (Table see page 437.)

For deciding now, if there is in India much or few U. V. in the sunlight, we must compare our results with those of other places on earth. As already has been mentioned only few measurements have been performed which make possible a comparison of the intensity and extension of the U. V. in the spectrum of the sun on different places on earth.

As to Davos known by his splendid climate DORNO [5]) has given tables of the average daily change of the shortest wavelength observable in the sunlight. Only in the months of April untill and inclusive of September wavelenghts shorter than 3000 ÅE. have been observed. The most favourable months at Davos are those of July and August and then the shortest wavelength observed on the average is 2969 ÅE., but only for one hour each day.

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[1]) Those months are just the most unfavourable of the year for the total radiation of the sun.

[2]) CH. FABRY and H. BUISSON: Astrophys. Journal **54**, 297—322, 1921.

[3]) G. M. B. DOBSON c.s. Proc. Royal Soc. London **110**, 660—693, 1926. **114**, 521—541, 1927.

[4]) CH. FABRY and H. BUISSON: Astrophys. Journal **54**, 297—322, 1921.

[5]) C. DORNO: Studie über Licht und Luft des Hochgebirges 1911, p. 107.

Wavelength in Å. E.	Intensity on earth	Absorption coefficient in ozone
2922	2.2	—
2931	5.5	11.2
2936	11	10.5
2946	25	9.3
2956	76	8.1
2963	132	7.4
2997	1320	4.7
3022	2700	3.4
3052	10200	2.3
3104	15100	—
3143	22400	0.7

Considering the results of DOBSON and HARRISON [1]) we see that in the English low-lying plain the ultra violet does not extend farther than to 2988 ÅE. The exposures have not been made in the most favourable part of the year, but on the other hand DOBSON and HARRISON must have been able to measure much farther in the U. V. by means of their very selective chlorine-bromine filters, because they have no inconvenience of an over-exposed visible part, nor of the inconvenient fogging in the U. V.

From the measurements of FABRY and BUISSON [2]) it is hardly impossible to deduce conclusions about the extension of the U. V. in the spectrum of the sun. The beautiful plate, printed opposite page 322, they got by using in the region below 2990 ÅE. no, between 2990 and 3040 ÅE. one and between 3040 and 3150 ÅE. two filters. More over the part of shortest wavelengths in this small region has been exposed for a longer time than the parts with longer wavelengths. The exposure has been made in Marseille, at the beginning of June and at about twelve o' clock, thus again at the most favourable momentum of the year and grace to the remedies mentioned above one can see yet traces of the line 2910 ÅE.

Herewith the materials, with which we would be able to compare, are exhausted. It is rather unextensive, but sufficient for concluding that the tropical sunlight has much ultra violet. This is also in good accordance with the results of the measurements about the quantity of ozone in the upper layers of the atmosphere, which have begun to be made in the tropical zones [3]). DOBSON c.s. find in Table Mt. (California), Helwan (Egypt) and

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[1]) G. M. B. DOBSON and D. N, HARRISON: Proc. Royal Soc. London **110**, 660—693, 1926.

[2]) CH. FABRY and H. BUISSON: Astrophys. Journal **54**, 297—322, 1921.

[3]) G. M. B. DOBSON, D. N. HARRISON and J. LAWRENCE: Proc. Royal Soc. London **122**, 456—486, 1929.

Kodai kanal (British India) the thickness of the absorbing layer of ozone to about 0.210 cm., thus only 70 % of the normal layer of ozone in moderate zones.

In the following tables the results are gathered, deduced from the photograms made at Amsterdam. The limits given are absorption lines. This absorption can only be noticed, when without these lines there is yet light of shorter wavelengths. This already weak intensity decreases however so continually, that the true limit of the spectrum of the sun is difficult to fix. For avoiding that our values might be uncertain, we have rather chosen the limits too much in the region of longer wavelenghts, than too far to shorter wavelenghts. Thus the limits fixed in this way are surely not too low.

BATAVIA—WELTEVREDEN.

August 9. 1928	12 o'clock	until 2948 AE.	(possibly untill 2941) with Ag-filter
„ 31. 1928	10 „	„ 2954 „	
Sept. 26. 1928	10 „	„ 2941 „	
Oct. 15. 1928	1 „	„ 2954 „	

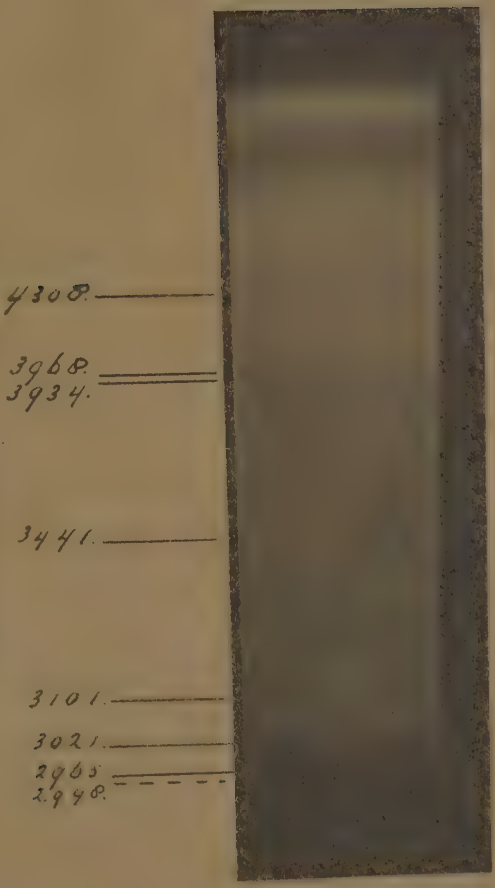
Tjibodas (1400 M.)

Oct. 3. 1928	11.30 „	„ 2954 „	with Ag-filter
„ „	11.30 „	„ 2948 „	
„ „	12.00 „	„ 2948 „	
„ „	12.30 „	„ 2948 „	exposed 10 sec.
„ „	12.30 „	„ 2936 „	exposed 20 sec.
„ 5. 1928	12.15 „	„ 2954 „	
„ „	12.35 „	„ 2948 „	
„ „	1.05 „	„ 2954 „	
„ 6. 1928	11.10 „	„ 2954 „	(possibly untill 2948)
„ „	11.40 „	„ 2954 „	
„ „	12.07 „	„ 2954 „	
„ „	12.23 „	„ 2948 „	(possibly untill 2941)

On a journey to the top of the Pangerango (3000 m.) no serviceable spectrograms could be made in consequence of the unfavourable weather.

The analysis of the photometer diagrams has been made possible by photographing the spectrum of a mercury arc over a number of sunspectra. From the known wavelengths of the mercury arc the dispersion curve could

J. C. BOEREMA and M. P. VRIJ: THE ULTRA VIOLET RADIATION IN TROPICAL SUNLIGHT.



Spectrum of the sun. (Tjibodas) $4\frac{1}{2}$ × enlarged.

Proceedings Royal Acad. Amsterdam. Vol. XXXII. 1929.

Kodai kanal (British India) the thickness of the absorbing layer of ozone to about 0.210 cm., thus only 70 % of the normal layer of ozone in moderate zones.

In the following tables the results are gathered, deduced from the photograms made at Amsterdam. The limits given are absorption lines. This absorption can only be noticed, when without these lines there is yet light of shorter wavelengths. This already weak intensity decreases however so continually, that the true limit of the spectrum of the sun is difficult to fix. For avoiding that our values might be uncertain, we have rather chosen the limits too much in the region of longer wavelenghts, than too far to shorter wavelenghts. Thus the limits fixed in this way are surely not too low.

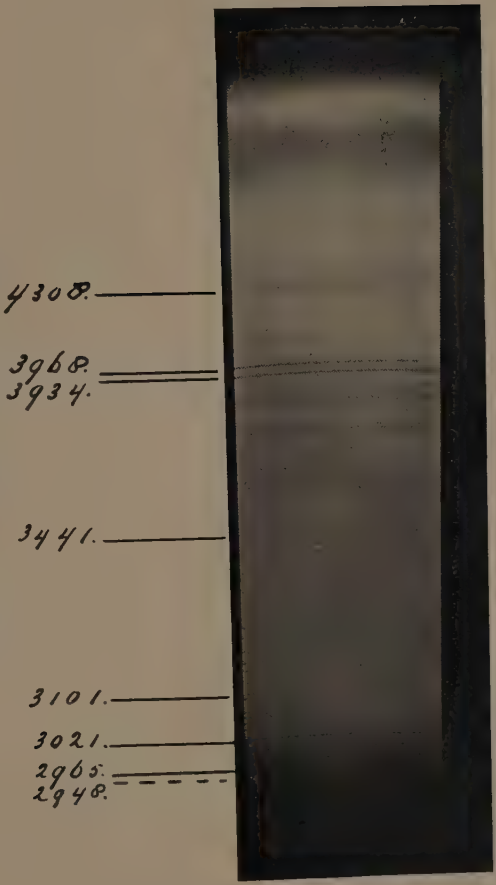
BATAVIA—WELTEVREDEN.

August 9. 1928	12 o'clock	until 2948 AE.	(possibly untill 2941) with Ag-filter
„ 31. 1928	10 „	„ 2954 „	
Sept. 26. 1928	10 „	„ 2941 „	
Oct. 15. 1928	1 „	„ 2954 „	
Tjibodas (1400 M.)			
Oct. 3. 1928	11.30 „	„ 2954 „	with Ag-filter
„ „	11.30 „	„ 2948 „	
„ „	12.00 „	„ 2948 „	
„ „	12.30 „	„ 2948 „	exposed 10 sec.
„ „	12.30 „	„ 2936 „	exposed 20 sec.
„ 5. 1928	12.15 „	„ 2954 „	
„ „	12.35 „	„ 2948 „	
„ „	1.05 „	„ 2954 „	
„ 6. 1928	11.10 „	„ 2954 „	(possibly untill 2948)
„ „	11.40 „	„ 2954 „	
„ „	12.07 „	„ 2954 „	
„ „	12.23 „	„ 2948 „	(possibly untill 2941)

On a journey to the top of the Pangerango (3000 m.) no serviceable spectrograms could be made in consequence of the unfavourable weather.

The analysis of the photometer diagrams has been made possible by photographing the spectrum of a mercury arc over a number of sunspectra. From the known wavelengths of the mercury arc the dispersion curve could

J. C. BOEREMA and M. P. VRIJ: THE ULTRA VIOLET RADIATION IN TROPICAL SUNLIGHT.



Spectrum of the sun. (Tjibodas) $4^1/_2$ × enlarged.

Proceedings Royal Acad. Amsterdam. Vol. XXXII. 1929.

be determined and by its means the wavelengths of the absorption lines in the spectrum of the sun. These lines could be identified by means of the absorption lines observed by FABRY and BUISSON [1]), so that thereafter the more accurate values of FABRY and BUISSON were taken for their wavelengths.

It is remarkable how little difference the exposures of Tjibodas (height 1400 m.) show with those of Batavia—Weltevreden. A consideration of the table on page 437 shows however that a rather large increase of intensity of the U. V. is necessary to observe an extension of the U. V. with some A.E. Also FABRY and BUISSON [2]) found this small extension of the spectrum to the side of short wavelengths with increasing height.

Some exposures have been taken with a small chemically silvered quartz plate (thickness 2 mm.) placed before the slit of the spectrograph. This gave clearly less fogging in the U. V. and was therefore more favourable for making photograms, but it is not yet certain whether it is possible to conclude to a further extension in the U. V.

One can expect that the intensity of the U. V. radiation of the sun is connected with the intensity of the total radiation of the sun. Since 1915 one of us (B.) has made observations by means of a "silverdisk" and a "Michelson" pyrheliometer and it appears, that with equal height of the sun (41.7°) the radiation at Batavia is averagely 6 % less than at Washington. This difference however is compensated by the averagely higher altitude of the sun at Batavia. The intensity of radiation at 12 o' clock at Batavia is averagely 3 % greater than at Washington.

The intensity at Batavia is smallest in the dry monsoon and decreases with increasing dryness and the duration of the East monsoon.

The minimum was 1.13 cal. [3]) (in the months of August and September), the maximum amounted to 1.30 cal. (in the months of December till May). All reduced on 60° height of the sun.

On higher lying places the radiation is greater. The values averagely found for different heights are:

at Batavia		1.25 cal.
at Tjisoeroepan	(1200 m.)	1.45 cal.
on the Pangerango	(3020 m.)	1.65 cal.
on the Smeroe	(3670 m.)	1.7 cal. [4])

Physical Laboratory of the
Medical University.

Batavia, March 1929.

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[1]) CH. FABRY and H. BUISSON: Astrophys. Journal **54**, 297—322, 1921.

[2]) CH. FABRY and H. BUISSON: Astrophys. Journal **54**, 297—322, 1921.

[3]) J. BOEREMA: Hand. 1e Ned. Ind. Natuurw. Congres 1919 p. 99—101.

[4]) All this is total sun radiation, of which the U.V. radiation is not more than 1%.

Comparative physiology. — *Das p_H-Optimum des Trypsins und die Reaktion des Darminhaltes.* Von H. J. Vonk und H. P. Wolvekamp. (Communicated by Prof. H. J. Jordan.)

(Communicated at the meeting of April 27, 1929).

Bisher hat man ziemlich allgemein angenommen, dass Trypsin und auch Erepsin im Darminhalt unter optimalen Bedingungen arbeiten. In der Uebereinstimmung zwischen dem p_H des Darminhaltes mit der Lage der Optima, welche beide auf etwa 8—8.5 angenommen wurden, sah man eine biologische Anpassung. Es wurde dabei allerdings vergessen, dass eine derartige Anpassung nicht zu gleicher Zeit für die Pankreasamylase bestehen kann, da ihr Optimum anders ist als dasjenige von Trypsin und Erepsin; es liegt bei p_H 6.8.

Dass man die Reaktion des Darminhaltes als alkalisch betrachtete, findet seinen Grund erstens in älteren Beobachtungen mittels Indikatoren, welche nicht zuverlässig sind und zweitens in einer Abhandlung von Auerbach und Pick [1]). Diese Autoren fanden Pankreas- und Darmfistelsaft bei elektrometrischer Messung alkalisch und sie zogen daraus den Schluss, dass auch der Dünndarminhalt alkalisch sein müsse, eine irrtümliche Schlussfolgerung, welche leider in die Literatur Eingang gefunden hat. Nun sind seit etwa 1915 von vielen amerikanischen Forschern [2]) elektrometrische Messungen des Darminhaltes gemacht worden und es stellte sich dabei heraus, dass der Darminhalt keineswegs alkalisch ist. In einigen Fällen, z.B. beim Säugling, beim Hunde und bei der Ratte [3]) soll der Darm durchweg über seine ganze Länge sauer sein, bei anderen Tieren findet man als Mittelwert p_H 7; die Abweichungen nach der alkalischen Seite sind ungefähr ebenso gross und häufig als die nach der sauren.

Auch die Meinung dass Trypsin sein Optimum bei p_H 8 oder höher hat, blieb nicht unwidersprochen. Man fand Substrate wofür es niedriger liegt [für Casein bei 6.5 [4])]. Diese Substrate werden also im Darme von Trypsin tatsächlich bei ihrem Optimum angegriffen.

Wir haben versucht die Frage zu lösen, wie es möglich ist, dass die Verdauung von Substraten (z.B. Fibrin) für welche das Optimum bei p_H 8 liegt, mit genügender Schnelligkeit verlaufen kann. Um diese Frage zu beantworten, ist es erstens notwendig zu wissen wie gross der Unterschied ist, den man in vitro beobachtet zwischen der Verdauungsintensität bei p_H 8 (Optimum) und 7 (Mittl. p_H des Darmes). Diese Frage kann beantwortet werden durch die Bestimmung des p_H-Optimums für eine etwa physiologische Zeitdauer von beispielsweise 2—6 Stunden. Wir haben derartige Bestimmungen ausgeführt für Fibrin und für Pepton-Witte und fanden, dass für Fibrin der Mehrumsatz bei p_H 8 etwa ein Drittel ist vom Gesamtumsatz bei p_H 7. Für Pepton ist der Unterschied zwischen der Wirkung beim Optimum (p_H 7.3) und bei p_H 7 sehr gering und die Lage des Optimums derart, dass bei 7 die Wirkung sogar stärker ist wie bei 8 [1]). Für letzteres Substrat ist es also ziemlich gleichgültig an welchem Punkte zwischen 7 und 8 die Wirkung stattfindet. Unterhalb 7 wird sie beträchtlich kleiner.

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[1]) Arb. a. d. Kaiserl. Gesundheitsamte Bd. **43**, S. 155 (1912).

[2]) Long and Fenger: Journ. Am. Chem. Soc. Bd. **39**, S. 1278 (1917); weiter Arbeiten von Mc Clendon u. a. Siehe z. B. die Literatur zitiert in E. Mislowitzer: Die Bestimmung der Wasserstoff-ionenkonzentration von Flüssigkeiten (Springer 1928) auf S. 360.

[3]) Für die Ratte wurde dies neuerdings gefunden von Mc Robert, G. R.: Ind. J. med. Res. Bd. **16**, S. 545 (1928).

[4]) Long, J. H. and Hull, M.: Journ. Am. Chem. Soc. Bd. **39**, S. 1051 (1917).

Wir konnten nun weiter zeigen, dass der Unterschied in der Wirkung, welchen man für Fibrin zwischen 7 und 8 findet, sehr unbedeutend ist verglichen mit dem Einfluss, welchen einige andere Faktoren auf die absolute Wirkungsgrösse dieses Enzymes ausüben. Derartige Faktoren können von zweierlei Art sein, d.h. von nicht-spezifischer oder von spezifischer Wirkung.

Als ersten (nicht-spezifischen) Faktor erkannten wir die Bewegung des Darminhaltes, welche künstlich durch Rühren des Gemisches nachgeahmt wurde. Eine mässige Rührgeschwindigkeit von etwa 45 Umdr. p. Min. steigerte in 5 Versuche den Umsatz auf das doppelte; in weiteren zwei Versuchen bei 90 Umdr. um das 2½ fache. Natürlich dürfte eine solche Bewegung den Umsatz beim Optimum auch noch steigern, daher nennen wir diesen Faktor nichtspezifisch.

Ein zweiter (nichtspezifischer) Faktor, den wir noch nicht untersuchten, ist der Einfluss den die Abfuhr der Spaltungsprodukte durch Resorption (nach zu ahmen durch Dialyse) wahrscheinlich haben wird.

Wir untersuchten weiter den Einfluss der Galle auf die Verdauung von Fibrin durch Trypsin und zwar bei p_H 6 in acht verschiedenen Volumkonzentrationen von $^1/_4$ bis $^1/_{20000}$. Bei Volumkonzentrationen von $^1/_4$ bis $^1/_{40}$ fanden wir eine Steigerung des Umsatzes bis um das zweifache. (S. Fig. 1.) Frühere Autoren haben an der sauren Seite nicht mit verschiedenen Konzentrationen der Galle gearbeitet. Es widersprechen sich die Angaben der Literatur. Geringere Konzentrationen als die genannten optimalen haben einen hemmenden Einfluss auf die Trypsinverdauung. Der Einfluss der Galle ist den gallensauren Salzen zuzuschreiben, wie sich aus ähnlichen Versuche ergab, die mit Natriumtaurocholat angestellt wurden.

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[1]) Für die Form der Optimumkurven, sowie für die Diskussion der abweichenden Resultate von MICHAELIS und DAVIDSOHN, verweisen wir auf unsere ausfürhliche Mitteilung in der Zs. f. physiol. Chemie.

Ob der Einfluss der Galle spezifisch ist für die Bedingungen der Darmverdauung würde sich mit Sicherheit nur entscheiden lassen wenn man auch

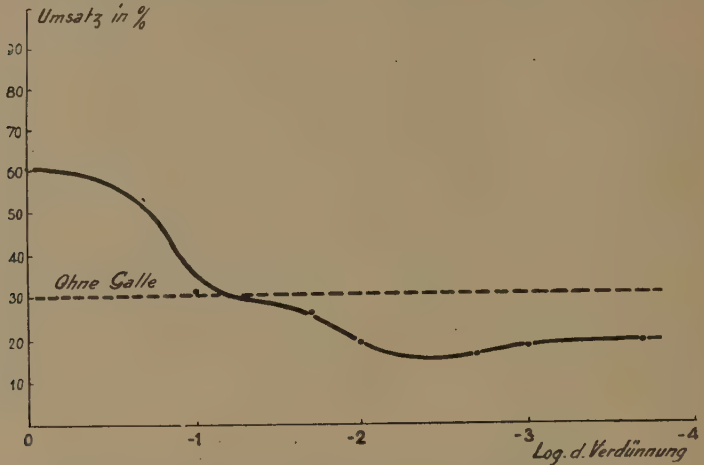

Fig. 1. Einfluss verschiedener Konzentrationen von Galle auf die Verdauung von Fibrin bei p_H 6. Die Verdünnungen sind die der zugesetzten Gallenmenge. Die Konzentrationen in der Versuchsflüssigkeit sind viermal kleiner.

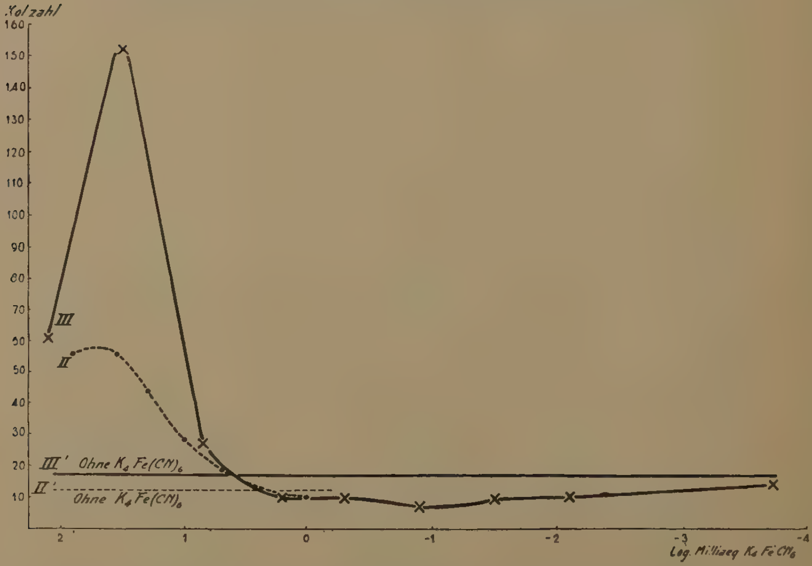

Fig. 2. Einfluss verschiedener Konzentrationen von $K_4Fe(CN)_6$ auf die Verdauung von Fibrin bei p_H 6 und 6.2. Die Konzentrationen sind hier bezogen auf das Volumen der Versuchsflüssigkeit.

für verschiedene andere p_H - Werte derartige Reihenversuchen anstellen würde. Dieses wäre eine sehr zeitraubende Arbeit; darum haben wir vorläufig diese Versuche noch nicht ausführen können.

Die folgenden Versuche liefern jedoch ein Argument zu Gunsten der Auffassung, dass die Galle „spezifisch" wirkt, d.h. den Einfluss des niederen p_H *kompensiert.*

Wir fanden nämlich, dass polyvalente Anionen einen gleichen Einfluss haben als die Galle. Auch dieser Einfluss wurde für $K_4 Fe (CN)_6$ bei p_H 6 für viele verschiedenen Konzentrationen untersucht. Dass dieser Einfluss wahrscheinlich sowohl für Galle als für das Blutlaugensalz in einen umladenden Wirkung besteht, welche sonst bei dem Optimum (p_H 8) von den OH-Ionen ausgeübt wird gibt uns einen Grund anzunehmen, dass dieser Einfluss der Galle wirklich spezifisch ist für den p_H des Darmes. (S. Fig. 2.)

Gegenüber den Einflüssen der Bewegung und der Aktivation durch Galle für die absolute Wirkungsgrösse des Trypsins tritt der Unterschied zwischen der Wirkung beim Optimum und beim mittleren p_H des Darmes stark zurück. Es ergibt sich aus alledem, dass die biologische Bedeuting des alkalischen Wirkungsoptimums von Trypsin stark überschätzt worden ist.

Institut für vergleichende Physiologie.

Utrecht, April 1929.

Mechanics. — *On the general theory of elastic stability.* (Third communication). By C. B. BIEZENO and H. HENCKY. (Communicated by Prof. W. VAN DER WOUDE).

(Communicated at the meeting of April 27, 1929).

In our first communication on the general problem of elastic stability (cf. these Proceedings, Vol. **31**, p. 569, 1928) we derived the differential equations which have to be fulfilled by the so called "additional stress components" $s_x, s_y, s_z, t_x, t_y, t_z$ that will bring an elastic body from a given state of stress (I) into another state (II) differing from the former one only by an infinitely small amount. The deduction of the equations was given in such a way that the relations which had to be assumed between these additional stresses and the strains produced by them were introduced only at the end of the calculations. The exact form of these relations is to a certain degree still a matter of speculation; in the paper mentioned before the authors wrote them as follows:

$$s_x = 2\,G\,.\frac{\partial u}{\partial x} + \frac{2\,G}{m-2}.\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right) \qquad \textit{cycl.}$$

$$t_x = 2\,G\,.\,f_x \qquad \textit{cycl.}$$

though they were fully aware of the arbitrariness of this special choice (comp. footnote l.c. p. 574).

Though the fact that several results obtained in this way were identical with results known from other sources, may be considered as an a posteriori justification of this choice, there remained the problem

a. to enunciate a stress relation which takes into account that the specific deformations in general will be *finite* (though they will be small compared to unity), and

b. to give this relation in a form applicable to the calculation of the "additional stress components" $s_x, \ldots t_x \ldots$

In the following paper we intend to give a solution of this problem.

In order to do this we shall distinguish between three states of our elastic body:

1. the state in which all stresses are absent, to be denoted by (0);
2. the stressed state (I), considered in our former paper;
3. the stressed state (II), considered in our former paper.

In all these states the coordinates of a material point will be referred to the same system of axes (to be called the "general system"), and will be denoted resp.

in state (0) by: $x_0 = x - U, \quad y_0 = y - V, \quad z_0 = z - W$

in state (I) by: $x, \quad y, \quad z$

in state (II) by: $\bar{x} = x + u, \quad \bar{y} = y + v, \quad \bar{z} = z + w.$

2. *The strains.*

In the first place we consider the transformation of the space in the neighbourhood of a given point of the body, which undergoes the transition from state (0) to state (I). Differentiating the coordinates x_0, y_0, z_0 we get:

$$\left.\begin{aligned} dx_0 &= \left(1 - \frac{\partial U}{\partial x}\right).dx - \frac{\partial U}{\partial y}.dy - \frac{\partial U}{\partial z}.dz \\ dy_0 &= -\frac{\partial V}{\partial x}.dx + \left(1 - \frac{\partial V}{\partial y}\right).dy - \frac{\partial V}{\partial z}.dz \\ dz_0 &= -\frac{\partial W}{\partial x}.dx - \frac{\partial W}{\partial y}.\partial z + \left(1 - \frac{\partial W}{\partial z}\right).dz \end{aligned}\right\} . \quad (1)$$

or solving for dx, dy, dz:

$$\left.\begin{aligned} dx &= (1 + a_{11}).dx_0 + a_{12}.dy_0 + a_{13}.dz_0 \\ dy &= a_{21}.dx_0 + (1 + a_{22}).dy_0 + a_{23}.dz_0 \\ dz &= a_{31}.dx_0 + a_{32}.dy_0 + (1 + a_{33}).dz_0 \end{aligned}\right\} . \quad (2)$$

If the derivatives of U, V, W with respect to x, y, z may be supposed to be very small compared to unity, the coefficients $a_{11}\ldots$ may be equalled to:

$$\left.\begin{aligned} a_{11} &= \frac{\partial U}{\partial x}, \quad a_{12} = \frac{\partial U}{\partial y}, \quad a_{13} = \frac{\partial U}{\partial z} \\ a_{21} &= \frac{\partial V}{\partial x}, \quad a_{22} = \frac{\partial V}{\partial y}, \quad a_{23} = \frac{\partial V}{\partial z} \\ a_{31} &= \frac{\partial W}{\partial x}, \quad a_{32} = \frac{\partial W}{\partial y}, \quad a_{33} = \frac{\partial W}{\partial z} \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (3)$$

In the second place we consider the transformation of the neighbourhood of the same point during the transition from state (I) to state (II).

Putting:

$$b_{11} = \frac{\partial u}{\partial x}, \quad b_{12} = \frac{\partial u}{\partial y}, \quad b_{13} = \frac{\partial u}{\partial z} \text{ etc.} \quad \ldots\ldots\ldots \quad (4)$$

this transformation is given by:

$$\left.\begin{aligned} \overline{dx} &= (1 + b_{11})\,dx + b_{12}.dy + b_{13}.dz \\ \overline{dy} &= b_{21}.dx + (1 + b_{22}).dy + b_{23}.dz \\ \overline{dz} &= b_{31}.dx + b_{32}.dy + (1 + b_{33}).dz \end{aligned}\right\} \quad \ldots \quad (5)$$

The combination of the equations (5) and (2) gives us the relation between the quantities $\overline{dx}$, $\overline{dy}$, $\overline{dz}$ and dx_0, dy_0, dz_0; using the abbreviations:

$$c_{mn} = b_{mn} + a_{mn} + b_{mk} \cdot a_{kn} = b_{mn} + a_{mn} + b_{m1}\, a_{1n} + b_{m2}\, a_{2n} + b_{m3}\, a_{3n}$$

this relation can be written:

$$\left.\begin{aligned} \overline{dx} &= (1+c_{11})\, dx_0 + c_{12} \cdot dy_0 + c_{13} \cdot dz_0 \\ \overline{dy} &= c_{21} \cdot dx_0 + (1+c_{22}) \cdot dy_0 + c_{23} \cdot dz_0 \\ \overline{dz} &= c_{31} \cdot dx_0 + c_{32} \cdot dy_0 + (1+c_{33})\, dz_0 \end{aligned}\right\} \quad \ldots \quad (6)$$

With the aid of the coefficients a_{mn}, resp. c_{mn}, the "strain-components"[1] defining the deformation of the neighbourhood of the point under consideration, during the transition 0—I, resp. 0—II, may be expressed by:

$$\left.\begin{aligned} \varepsilon^I_x &= a_{11} + \tfrac{1}{2} \cdot (a^2_{11} + a^2_{21} + a^2_{31}) \\ \gamma^I_x &= \tfrac{1}{2}\,(a_{23} + a_{32} + a_{12}\, a_{13} + a_{22}\, a_{23} + a_{32}\, a_{33}) \end{aligned}\right\} \quad \ldots \quad (7^a)$$

$$\left.\begin{aligned} \varepsilon^{II}_x &= c_{11} + \tfrac{1}{2} \cdot (c^2_{11} + c^2_{21} + c^2_{31}) \\ \gamma^{II}_x &= \tfrac{1}{2}\,(c_{23} + c_{32} + c_{12}\, c_{13} + c_{22}\, c_{23} + c_{32}\, c_{33}) \end{aligned}\right\} \, ^{1)} \quad \ldots \quad (7^b)$$

The meaning of these quantities may be elucidated by introducing the so called inverse strain ellipsoids, the equations of which are resp.:

$$(1+2\varepsilon^I_x) \cdot x^2 + (1+2\varepsilon^I_y) \cdot y^2 + (1+2\varepsilon^I_z) \cdot z^2 + 4\gamma^I_x \cdot yz + 4\gamma^I_y \cdot zx + 4\gamma^I_z \cdot xy = 1 \quad (8^a)$$

$$(1+2\varepsilon^{II}_x) \cdot x^2 + (1+2\varepsilon^{II}_y) \cdot y^2 + (1+2\varepsilon^{II}_z) \cdot z^2 + 4\gamma^{II}_x \cdot yz + 4\gamma^{II}_y \cdot zx + 4\gamma^{II}_z \cdot xy = 1 \quad (8^b)$$

Both of them have the point x_0, y_0, z_0 as center; the equations refer to axes passing through this point and having the same directions as the general system of coordinates. When the length of an element passing in a given direction through the point x_0, y_0, z_0 in state (0) is called ds_0, and the length of the same element in state (I), resp. (II), is called ds_I, resp. ds_{II}, then the quotient $\frac{ds_I}{ds_0}$, resp. $\frac{ds_{II}}{ds_0}$ will be given by the reciprocal of the radius vector of the first, resp. the second, ellipsoid, drawn from the center in the direction of ds_0.

The deformation of the neighbourhood of the point x_0, y_0, z_0 is fully defined by the magnitude and the directions of the principal axes of the strain ellipsoid (8^a), resp. (8^b).

When now we wish to make a picture of the deformation $0 - \mathrm{I}$ in the point x, y, z of the body in state I, in stead of in the point x_0, y_0, z_0, then we have to bear in mind that the transformation of space which governs the whole of the transition from 0 to I, is composed not only of the deformation described above, but also of the translation from x_0, y_0, z_0 to x, y, z (which for our purpose has no special meaning), and of a rotation Ω, the components of which are

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[1] Cf.: A. E. H. LOVE. A treatise of the mathematical theory of elasticity. 4th edition. 1927. p. 60 and 66.

$$\Omega_x = \frac{1}{2} \cdot \left(\frac{\partial W}{\partial y} - \frac{\partial V}{\partial z} \right) \qquad \textit{cycl.}$$

The axes of the inverse strain ellipsoid have to take part in this rotation. Hence we shall get the equation of this ellipsoid with respect to axes passing through the point x, y, z and having the directions of the axes of the general coordinate system, when in the point x_0, y_0, z_0 we describe the ellipsoid with respect to a system of axes, turned backwards over the angle Ω. Denoting these new axes by x', y', z' the corresponding transformation of coordinates is defined by a scheme of the form:

$$\begin{array}{cccc} & x & y & z \\ x' & l_1 & m_1 & n_1 \\ y' & l_2 & m_2 & n_2 \\ z' & l_3 & m_3 & n_3 \end{array}$$

in which the coefficients are approximately equal to those of the scheme:

$$\begin{array}{cccc} & x & y & z \\ x' & 1 & -\Omega_z & +\Omega_y \\ y' & +\Omega_z & 1 & -\Omega_x \\ z' & -\Omega_y & +\Omega_x & 1 \end{array}$$

Hence the equation of the ellipsoid (8^a) with respect to the new system becomes:

$$(1+2\varepsilon_x^I)(l_1x'+l_2y'+l_3z')^2 + (1+2\varepsilon_y^I)(m_1x'+m_2y'+m_3z')^2 +$$
$$+(1+2\varepsilon_z^I)(n_1x'+n_2y'+n_3z')^2 + 4\gamma_x^I(m_1x'+m_2y'+m_3z')(n_1x'+n_2y'+n_3z') +$$
$$+ 4\gamma_y^I(n_1x'+n_2y'+n_3z')(l_1x'+l_2y'+l_3z') +$$
$$+ 4\gamma_z^I(l_1x'+l_2y'+l_3z')(m_1x'+m_2y'+m_3z') = 1.$$

The approximations $1, +\Omega_z, -\Omega_y \ldots$ for $l_1, l_2, l_3 \ldots$ may be introduced only after the equation has been reduced as far as possible by using the orthogonality-relations between $l_1, l_2 \ldots$

The coefficients of the equation thus obtained may be considered as the strain-components which define the deformation in the neighbourhood of the point x, y, z arising from the transition 0 — I, when this deformation is described with respect to a system of axes passing in the normal directions through x, y, z. Calling these the strain-components e^I_x, e^I_y, e^I_z, g^I_x, g^I_y, g^I_z we have the formulae:

$$e^I_x = \varepsilon^I_x - 2\,(\Omega_z\,\gamma^I_z - \Omega_y\,\gamma^I_y) \qquad \textit{cycl.}$$

$$g^I_x = \gamma^I_x - [\Omega_x\,(\varepsilon^I_z - \varepsilon^I_y) + \Omega_y\,\gamma^I_z - \Omega_z\,\gamma^I_y] \qquad \textit{cycl.}$$

Coming now to the deformation, arising from the transition I—II, we remark that this deformation can be found by considering the differences in shape and position of the two ellipsoids (8^a) and (8^b) in the point x_0, y_0, z_0. When it is desired to get a picture of this deformation in the neighbourhood of the point x, y, z of the body in state I, we have only to rotate these two ellipsoids together over the angle Ω, taking care that their relative position does not change. The equation of the second ellipsoid after the rotation, referred to a normally orientated system of coordinates, is:

$$(1+2e^{II}_x)\,x^2 + (1+2e^{II}_y)\,y^2 + (1+2e^{II}_z)\,z^2 + 4\,g^{II}_x\,yz + 4\,g^{II}_y\,zx + 4\,g^{II}_z\,xy = 1$$

where the quantities e^{II}_x, e^{II}_y, e^{II}_z, g^{II}_x, g^{II}_y, g^{II}_z have the values:

$$e^{II}_x = \varepsilon^{II}_x - 2\,(\Omega_z\,\gamma^{II}_z - \Omega_y\,\gamma^{II}_y) \qquad \textit{cycl.}$$

$$g^{II}_x = \gamma^{II}_x - [\Omega_x\,(\varepsilon^{II}_z - \varepsilon^{II}_y) + \Omega_y\,\gamma^{II}_z - \Omega_z\,\gamma^{II}_y]. \qquad \textit{cycl.}$$

If now we put:

$$e^{II}_x = e^I_x + \triangle e_x \qquad \textit{cycl.}$$

$$g^{II}_x = g^I_x + \triangle g_x \qquad \textit{cycl.}$$

then, using (6) and neglecting terms of the second and higher orders in the quantities b, we find for the quantities $\triangle e_x$ and $\triangle g_x$:

$$\left.\begin{aligned} \triangle e_x &= b_{11} + 2a_{11}\,b_{11} + \tfrac{1}{2}.(a_{12}+a_{21})\,(b_{12}+b_{21}) + \tfrac{1}{2}.(a_{13}+a_{31})\,(b_{13}+b_{31}) \quad \textit{cycl.} \\ \triangle g_x &= \tfrac{1}{2}.\{b_{23} + b_{32} + (a_{22}+a_{33})\,(b_{23}+b_{32}) + (a_{23}+a_{32})\,(b_{22}+b_{33}) \\ &\quad + \tfrac{1}{2}.(a_{12}+a_{21})\,(b_{13}+b_{31}) + \tfrac{1}{2}.(a_{13}+a_{31})\,(b_{12}+b_{21})\} \quad \textit{cycl.} \end{aligned}\right\}(9)$$

3. *The stress-strain-relations.*

As has been mentioned in N^0. 1, we have to keep in mind that the elastic body in state I has already suffered finite deformations, though in all practical cases these deformations will be small. This fact renders it necessary to introduce a new relation between strain and stress.

In order to reduce the freedom of choice which arises as soon as we depart from the ordinary HOOKE's law, we shall fix that the relation must fulfill the following conditions:

1. the change of the volume of an element of the elastic body depends only on the hydrostatic part of the stress system;

2. the specific elastic energy A, measured with respect to unit volume in the unstrained state 0, is equal to the sum of the energy due to the hydrostatic part of the stress system, and the energy due to the deviatoric part.

It may be shown that a system of relations, fulfilling these conditions, can be obtained, when we introduce the quantity:

$$ln \left\{ \frac{\textit{final length}}{\textit{original length}} \right\}$$ [1]

as the measure for the specific elongation of a linear element, and put:

$$2A = 2G \left\{ (\varepsilon_1 - \varepsilon)^2 + (\varepsilon_2 - \varepsilon)^2 + (\varepsilon_3 - \varepsilon)^2 \right\} + 9\, K\varepsilon^2$$

In this expression G and K are constants; ε_1, ε_2, ε_3 are the new-defined specific elongations in the directions of the principal axes of the strain (which of course coincide with the principal axes of the stress) and

$$\varepsilon = \tfrac{1}{3}\, (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)$$

Let S_1, S_2, S_3 be the principal stresses in a given point (measured with respect to unit area in the stressed state), dx_1, dx_2, dx_3 the original lengths of the sides of a rectangular element of volume, the faces of which are orientated normally to the principal stresses, $\overline{dx_1}$, $\overline{dx_2}$, $\overline{dx_3}$ the lengths of the sides in the stressed state, so that:

$$\varepsilon_1 = ln\, \frac{\overline{dx_1}}{dx_1}$$

$$\varepsilon_2 = ln\, \frac{\overline{dx_2}}{dx_2}$$

$$\varepsilon_3 = ln\, \frac{\overline{dx_3}}{dx_3}$$

then we may calculate the change δA of the specific elastic energy accompanying an arbitrary variation $\delta \overline{dx_1} \ldots$ of the strain either from the expression:

$$\delta A = 2G \left\{ (\varepsilon_1 - \varepsilon)\, \delta\, (\varepsilon_1 - \varepsilon) + (\varepsilon_2 - \varepsilon)\, \delta\, (\varepsilon_2 - \varepsilon) + (\varepsilon_3 - \varepsilon)\, \delta\, (\varepsilon_3 - \varepsilon) \right\} + 9K\, \varepsilon \delta \varepsilon$$

or from the work produced by the stresses S_1, S_2, S_3:

$$\delta A = \frac{1}{dx_1\, dx_2\, dx_3} \,.\, \left\{ S_1\, \overline{dx_2}\, \overline{dx_3}\, \delta\, \overline{dx_1} + S_2\, \overline{dx_3}\, \overline{dx_1}\, \delta\, \overline{dx_2} + S_3 \overline{dx_1}\, \overline{dx_2}\, \delta\, \overline{dx_3} \right\}$$

$$\delta A = \frac{\overline{dx_1}\, \overline{dx_2}\, \overline{dx_3}}{dx_1\, dx_2\, dx_3} \,.\, \left\{ S_1 \,.\, \frac{\delta \overline{dx_1}}{\overline{dx_1}} + S_2 \,.\, \frac{\delta \overline{dx_2}}{\overline{dx_2}} + S_3 \,.\, \frac{\delta \overline{dx_3}}{\overline{dx_3}} \right\}$$

$$\delta A = e^{3\varepsilon} \,.\, \left\{ S_1\, \delta\varepsilon_1 + S_2\, \delta\varepsilon_2 + S_3\, \delta\varepsilon_3 \right\}$$

$$\delta A = e^{3\varepsilon} \left\{ (S_1 - S)\, \delta\, (\varepsilon_1 - \varepsilon) + (S_2 - S)\, \delta\, (\varepsilon_2 - \varepsilon) + (S_3 - S)\, \delta\, (\varepsilon_3 - \varepsilon) \right\} + e^{3\varepsilon} \,.\, 3S \,.\, \delta\varepsilon$$

(in the latter expression we have written: $S = \frac{1}{3} \,.\, (S_1 + S_2 + S_3)$). As both results have to be equal for all values of the variations, we find:

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[1] Comp.: H. HENCKY. Ueber die Form des Elastizitätsgesetzes... Zeitschrift für technische Physik. 9. Jahrgang. 1928. S. 215—220. Berichtigung S. 457.

$$e^{3\varepsilon} \, . \, S_i = 2G(\varepsilon_i - \varepsilon) + 3K\varepsilon \quad (i = 1, 2, 3). \quad . \quad . \quad . \quad . \quad (10^a)$$

This formula gives for a pure hydrostatic state of stress:

$$e^{3\varepsilon} \, S = 3K \, . \, \varepsilon.$$

Hence the elastic law may be written:

$$\begin{aligned} e^{3\varepsilon} (S_i - S) &= 2G (\varepsilon_i - \varepsilon) \\ e^{3\varepsilon} \, S &= 3K\varepsilon \end{aligned}$$

or putting

$$e^{3\varepsilon} \, S_i = S_i{}'$$

$$S_i' - S' = 2G (\varepsilon_i - \varepsilon) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10^b)$$

$$S' = 3K\varepsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10^c)$$

The quantities S_i' may be called "reduced" principal stresses.

4. *The relations between the stress-components $S_x' \ldots T_x' \ldots$ and the strain-components $e_x \ldots g_x \ldots$*

Having found the connection between the reduced "principal stresses" S_i' and the corresponding quotients $\dfrac{\overline{dx_i}}{dx_i}$, we now shall deduce the relations existing between the quantities S_i' and the quantities e_i, i.e. the strain-components referring to the principal axes of the strain ellipsoid. We have:

$$\frac{\overline{dx_i}}{dx_i} = \sqrt{1 + 2e_i}$$

hence:

$$S_i{}' - S' = 2G \, . \, \{ \ln \sqrt{1 + 2e_i} - \tfrac{1}{6} \, . \, \ln \, (1 + 2e_1)(1 + 2e_2)(1 + 2e_3) \}$$

or developing with respect to the e's and neglecting all powers and products of the third degree and higher:

$$S_i{}' - S' = 2G \{ e_i - \tfrac{1}{3} \, . \, (e_1 + e_2 + e_3) - [e_i^2 - \tfrac{1}{3} \, . \, (e_1^2 + e_2^2 + e_2^3)] + \ldots \} \quad (11)$$

These relations only give the connection between principal stresses and principal strains. Now we introduce an arbitrary system of coordinates x', y', z', the position of which with respect to the system $x, y, z,$ defined by the principal stresses, is given by the scheme of coefficients:

$$\begin{array}{cccc} & x & y & z \\ x' & l_1 & m_1 & n_1 \\ y' & l_2 & m_2 & n_2 \\ z' & l_3 & m_3 & n_3 \end{array}$$

Then we get for the stress components, referred to the system x', y', z' the expressions:

$$S'_x = S'_1\, l_1^2 + S'_2\, m_1^2 + S'_3\, n_1^2 \qquad \textit{cycl.}$$

$$T'_x = S'_1\, l_2\, l_3 + S'_2\, m_2\, m_3 + S'_3\, n_2\, n_3 \qquad \textit{cycl.}$$

and for the components of the strain:

$$e_x = e_1\, l_1^2 + e_2\, m_1^2 + e_3\, n_1^2 \qquad \textit{cycl.}$$

$$g_x = e_1\, l_2\, l_3 + e_2\, m_2\, m_3 + e_3\, n_2\, n_3 \qquad \textit{cycl.}$$

It is known that e_1, e_2, e_3 are the roots of the equation:

$$\begin{vmatrix} e_x - e_i & g_z & g_y \\ g_z & e_y - e_i & g_x \\ g_y & g_x & e_z - e_i \end{vmatrix} = 0$$

Now we have:

$$S'_x - S' = (S'_1 - S')\, l_1^2 + (S'_2 - S')\, m_1^2 + (S'_3 - S')\, n_1^2.$$

Substituting from formulae (11) we get:

$$S'_x - S' = 2\, G\, \{[e_1\, l_1^2 + e_2\, m_1^2 + e_3\, n_1^2 - \tfrac{1}{3}\,.\,(e_1 + e_2 + e_3)]$$
$$- [(e_1\, l_1^2 + e_2\, m_1^2 + e_3\, n_1^2)^2 - \tfrac{1}{3}\,.\,(e_1^2 + e_2^2 + e_3^2)] \ldots\}$$

Finally, writing again $e = \frac{1}{3}(e_1 + e_2 + e_3)$ and making use of some well known properties of the invariants of quadratic surfaces, we get:

$$\left.\begin{array}{l} S'_x - S' = 2\, G\, \{e_x - e - [e_x^2 + g_z^2 + g_y^2 - \tfrac{1}{3}\,.\,(e_x^2 + e_y^2 + e_z^2 + \\ \qquad\qquad + 2 g_x^2 + 2\, g_y^2 + 2\, g_z^2)] \ldots\}\ \textit{cycl.} \end{array}\right\} \quad (12^a)$$

In the same way we obtain:

$$T'_x = 2\, G\, \{g_x - [g_x\,(e_y + e_z) + g_y\, g_z] \ldots\} \quad . \quad . \quad \textit{cycl.} \quad . \quad (12^b)$$

These formulae give us the expression of the deviatoric part of the stress system as a function of the strain-components.

For the hydrostatic part we have, as mentioned in the foregoing paragraph:

$$S' = 2\, G\, .\, \frac{m+1}{3\,(m-2)}\, .\, \left\{\frac{\partial U}{\partial x} + \frac{\partial V}{\partial y} + \frac{\partial W}{\partial z}\right\} . \quad . \quad . \quad . \quad (12^c)$$

We now return to our two states of stress I and II, and apply to each of them the expressions just found. Then, keeping in mind that these states differ only by infinitely small amounts, we get:

$$\left.\begin{aligned}&(S'_x - S')^{II} - (S'_x - S')^{I} = [(S'_x)^{II} - (S'_x)^{I}] - [(S')^{II} - (S')^{I}] = \\ &= 2\,G\,\{\triangle e_x - \triangle e - 2\,[e_x\,\triangle e_x + g_z\,\triangle g_z + g_y\,\triangle g_y - \\ &- \tfrac{1}{3}\,.\,(e_x \triangle e_x + e_y \triangle e_y + e_z \triangle e_z + 2g_x \triangle g_x + 2g_y \triangle g_y + 2g_z\,\triangle g_z)]\}\ \mathit{cycl.}\end{aligned}\right\}\quad (13^a)$$

$$\left.\begin{aligned}(T'_x)^{II} - (T'_x)^{I} = 2G\,\{\triangle g_x - [g_x\,(\triangle e_y + \triangle e_z) + \triangle g_x\,(e_y + e_z) + \\ + g_y\,\triangle g_z + g_z\,\triangle g_y]\}\ \mathit{cycl.}\end{aligned}\right\}\quad (13^b)$$

$$(S')^{II} - (S')^{I} = 2G\,.\,\frac{m+1}{3\,(m-2)}\,.\left\{\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right\}.\quad .\quad .\quad (13^c)$$

In order to abbreviate our formulae we shall write:

$$(S'_x)^{II} = \overline{S}'_x \quad , \quad (S'_x)^{I} = S'_x\,,$$
$$(T'_x)^{II} = \overline{T}'_x \quad , \quad (T'_x)^{I} = T'_x,$$

then a reduction by means of formula (9) finally gives us:

$$\overline{S}'_x - S'_x = 2\,G\left\{\frac{\partial u}{\partial x} + \frac{1}{m-2}\,.\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right)\right\}\ \mathit{cycl.}\quad .\quad (14^a)$$

$$\overline{T}'_x - T_x = 2\,G\,.\,f_x\,.\quad .\quad .\quad .\quad .\quad \mathit{cycl.}\quad .\quad (14^b)$$

$$\overline{S}' - S' = 2\,G\,.\,\frac{m+1}{3\,(m-2)}\,.\left\{\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right\}\quad .\quad .\quad .\quad .\quad (14^c)$$

In performing the reduction all quantities of orders higher than the second again have been neglected. The expressions (14) may be written:

$$\overline{S}'_x - S'_x = \sigma_x \quad .\ \mathit{cycl.}\ .\ .\ .\ .\ .\ .\quad (15^a)$$
$$\overline{T}'_x - T'_x = \tau_x \quad .\ \mathit{cycl.}\ .\ .\ .\ .\ .\ .\quad (15^b)$$
$$\overline{S}' - S' = \sigma \quad .\ .\ .\ .\ .\ .\ .\ .\ .\ .\quad (15^c)$$

where:

$$\sigma = \tfrac{1}{3}\,(\sigma_x + \sigma_y + \sigma_z)$$

5. *The relations between the quantities $S'_x \ldots T'_x \ldots$ and the stress-components $X_x \ldots Y_x \ldots Z_x \ldots,\ s_x \ldots t_x \ldots$ introduced in the first paper.*

Until now the following sets of quantities have been introduced:

$$S_x,\ S_y,\ S_z,\ T_x,\ T_y,\ T_z$$

which defines the stress system in state I, with respect to axes orientated parallel to the general coordinate system;

$$S'_x,\ S'_y,\ S'_z,\ T'_x,\ T'_y,\ T'_z$$

which defines the "reduced" stresses in the same state, and which are given by the expressions:

$$S'_x = \left(1 + \frac{\partial U}{\partial x} + \frac{\partial V}{\partial y} + \frac{\partial W}{\partial z}\right) . S_x \; cycl.$$

$$T'_x = \left(1 + \frac{\partial U}{\partial y} + \frac{\partial V}{\partial y} + \frac{\partial W}{\partial z}\right) . T_x \; cycl.;$$

$$\overline{S}_x, \overline{S}_y, \overline{S}_z, \overline{T}_x, \overline{T}_y, \overline{T}_z$$

which defines the stress system in state II with respect to a system of coordinates, coinciding with the normally orientated system in the point x, y, z but which, starting from this position has to be rotated over the angle $\triangle \Omega$ with components:

$$\triangle \Omega_x = \omega_x = \frac{1}{2}\left(\frac{\partial w}{\partial y} - \frac{\partial v}{\partial z}\right) \; cycl.$$

in order to arrive at the final position, belonging to state II;

$$\overline{S}'_x, \overline{S}'_x. \overline{S}'_z, \overline{T}'_x, \overline{T}'_y, \overline{T}'_z$$

the "reduced" stresses which can be derived from the foregoing quantities, by means of the equations:

$$\overline{S}'_x = \left(1 + \frac{\partial U}{\partial x} + \frac{\partial V}{\partial y} + \frac{\partial W}{\partial z}\right)\left(1 + \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right) . \overline{S}_x \; cycl.$$

$$\overline{T}'_x = \left(1 + \frac{\partial U}{\partial x} + \frac{\partial V}{\partial y} + \frac{\partial W}{\partial z}\right)\left(1 + \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right) . \overline{T}_x \; cycl.$$

To these four sets of stress components we add the system

$$\overline{S}^{\times}_x, \overline{S}^{\times}_y, \overline{S}^{\times}_z, \overline{T}^{\times}_x, \overline{T}^{\times}_y, \overline{T}^{\times}_z$$

which defines the (unreduced) stresses in state II with respect to a system of coordinate axes, passing through the point $\overline{x}, \overline{y}, \overline{z}$ and having directions parallel to the general system of coordinates (with respect to this latter system the axes connected with the quantities $S_x \ldots \overline{T}_x \ldots$ show the rotation $\triangle \Omega = \omega$).

This fifth system is defined by the relations:

$$\overline{S}^{\times}_x = \overline{S}_x - 2\,(\overline{T}_z\,\omega_z - \overline{T}_y\,\omega_y) \; cycl.$$

$$\overline{T}^{\times}_x = \overline{T}_x - [\omega_x\,(\overline{S}_z - \overline{S}_y) + \overline{T}_z\,\omega_y - \overline{T}_y\,\omega_z] \; cycl.$$

It presents no difficulty to formulate the connection between these latter quantities and the quantities $X_x \ldots Y_x \ldots Z_x \ldots$ introduced in our first paper. Both systems define one and the same state of stress in the point $\overline{x}, \overline{y}, \overline{z}$; the quantities $\overline{S}^{\times}_x \ldots \overline{T}^{\times}_x \ldots$, however, are related to surface elements which are orientated normally to the general system of coordinates, whereas $X_x \,.\,.\, X_x \,.\,.\, Z_x \,.\,.$ represent the components of the stress vectors acting on surface elements which in state I were orientated normally to these directions, so that in state II they in general will have a skew position.

In order to define these positions we introduce unit vectors $\overline{n}_x, \overline{n}_y, \overline{n}_z$ which are orientated normally to these elements, in such a way, that n_x is normal to that element in state II, which originally in state I was normal to the x-axis, and so on. The components of the vectors $\overline{n}_x, \overline{n}_y, \overline{n}_z$ are given by the scheme:

$$\begin{array}{cccc}
 & n_x & \overline{n}_y & \overline{n}_z \\
(x) & 1 & -\frac{\partial v}{\partial x}\cdot\left(1-\frac{\partial u}{\partial x}-\frac{\partial w}{\partial z}\right), & -\frac{\partial w}{\partial x}\cdot\left(1-\frac{\partial u}{\partial x}-\frac{\partial v}{\partial y}\right) \\
(y) & -\frac{\partial u}{\partial y}\cdot\left(1-\frac{\partial v}{\partial y}-\frac{\partial w}{\partial z}\right), & 1 & -\frac{\partial w}{\partial y}\cdot\left(1-\frac{\partial u}{\partial x}-\frac{\partial v}{\partial y}\right) \\
(z) & -\frac{\partial u}{\partial z}\cdot\left(1-\frac{\partial v}{\partial y}-\frac{\partial w}{\partial z}\right), & -\frac{\partial v}{\partial z}\cdot\left(1-\frac{\partial u}{\partial x}-\frac{\partial w}{\partial z}\right), & 1
\end{array}$$

If now $\overline{n}$ denotes the unit vector normal to an arbitrary element of surface in $\overline{x}, \overline{y}, z$, we have:

$$X_{\overline{n}} = \left[\overline{S}_x^{\times} \,.\, \cos(\overline{n}x) + \overline{T}_z^{\times} \,.\, \cos(\overline{n}y) + \overline{T}_x^{\times} \,.\, \cos(\overline{n}z)\right] . \, \varphi(\overline{n}) \;\; cycl.$$

where

$$\varphi(\overline{n}_x) = 1 + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \;\; cycl.$$

Hence specialising for $\overline{n}_x, \overline{n}_y, \overline{n}_z$:

$$X_x = \overline{S}_x^{\times}\left(1 + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right) - \overline{T}_z^{\times} \,.\, \frac{\partial u}{\partial y} - \overline{T}_y^{\times} \,.\, \frac{\partial u}{\partial z} \;\; cycl.$$

$$Y_x = \overline{T}_z^{\times}\left(1 + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right) - \overline{S}_y^{\times} \,.\, \frac{\partial u}{\partial y} - \overline{T}_x^{\times} \,.\, \frac{\partial u}{\partial z} \;\; cycl.$$

$$Z_x = \overline{T}_y^{\times}\left(1 + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right) - \overline{T}_x^{\times} \,.\, \frac{\partial u}{\partial y} - \overline{S}_z^{\times} \,.\, \frac{\partial u}{\partial z} \;\; cycl.$$

As the differences $(\overline{S}_x' - S_x')$ and $(\overline{S}_x^{\times} - S_x)$ etc. are infinitely small of the order of u, v, w we may — when we restrict ourselves in the future to quantities of the first order only — write $S_x \,.\, \frac{\partial u}{\partial x}$ instead of $\overline{S}_x^{\times} . \frac{\partial u}{\partial x}$ etc.

In this way we get the following system of equations:

$$\left.\begin{aligned}X_x&=\overline{S}_x^{\times}+S_x\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)-\left(S_x.\frac{\partial u}{\partial x}+T_z f_z+T_y f_y\right)+(T_z\,\omega_z-T_y\omega_y)\\Y_x&=\overline{T}_z^{\times}+T_z\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)-\left(T_z.\frac{\partial u}{\partial x}+S_y f_z+T_x f_y\right)+(S_y\,\omega_z-T_x\omega_y)\\Z_x&=\overline{T}_y^{\times}+T_y\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)-\left(T_y.\frac{\partial u}{\partial x}+T_x f_z+S_z f_y\right)+(T_x\omega_z-S_z\omega_y)\\&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\textit{cycl.}\end{aligned}\right\}\quad(16)$$

Making use now of the equations (5 *a*, *b*, *c*) of the first paper, which give a relation between the quantities $s_x \ldots t_x \ldots$ and $X_x \ldots Y_x \ldots Z_x \ldots$, we find (with the aid of (16)):

$$\left.\begin{aligned}s_x-\left(\overline{S}_x^{\times}-S_x\right)&=S_x\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)-\left(S_x\ldots\frac{\partial u}{\partial x}+T_z f_z+T_y f_y\right)+\\&\qquad+2\,(T_z\,\omega_z-T_y\,\omega_y)\ \textit{cycl.}\end{aligned}\right\}\quad(17^a)$$

$$\begin{aligned}t_x-\left(\overline{T}_x^{\times}-T_x\right)&=T_x\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)-\left(T_y f_z+T_x\,.\,\frac{\partial v}{\partial y}+S_z f_x\right)-\\&\qquad-r_x+\omega_x\,(S_z-S_y)+T_z\,\omega_y-T_y\,\omega_z\ \ \textit{cycl.}\end{aligned}$$

or using formula (4) of the first paper:

$$\left.\begin{aligned}&t_x-\left(\overline{T}_x^{\times}-T_x\right)=T_x\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)-\\&\frac{1}{2}\cdot\left\{(S_y+S_z)\,f_x+T_x\left(\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)+T_z f_y+T_y f_z\right\}+(S_z-S_y)\,\omega_x+T_z\omega_y-T_y\omega_z\\&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\textit{cycl.}\end{aligned}\right\}\quad(17^b)$$

Returning to the quantities:

$$\overline{S}_x'\ldots\overline{T}_x'\ldots\quad\text{and}\quad S_x'\ldots T_x'\ldots$$

we get:

$$s_x-(\overline{S}_x'-S_x')=-\left(S_x\,.\,\frac{\partial u}{\partial x}+T_z\,f_z+T_y\,f_y\right)\ \textit{cycl.}\quad .\quad(18^a)$$

$$t_x-(\overline{T}_x'-T_x')=-\tfrac{1}{2}\,.\left\{(S_y+S_z)\ f_x+T_x\left(\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)+T_z\,f_y+T_y\,f_z\right\}\quad(18^b)$$
$$\textit{cycl.}$$

or, on account of the relations found at the end of § 4 and of equation (4) of the first paper:

$$s_x=\sigma_x-\left(S_x\,.\,\frac{\partial u}{\partial x}+T_z\,f_z+T_y\,f_y\right)\ \textit{cycl.}\quad .\quad .\quad(19^a)$$

$$t_z-r_z=\tau_z-\left(S_x\ f_z+T_z\,.\,\frac{\partial v}{\partial y}+T_y\,f_x\right)\ \textit{cycl.}\quad .\quad(19^b)$$

$$t_y+r_y=\tau_y-\left(S_x\ f_y+T_z\,f_x+T_y\,.\,\frac{\partial w}{\partial z}\right)\ \textit{cycl.}\quad .\quad(19^c)$$

6. *The final equations.*

When the expressions (19) are substituted in the equations (6) of the first paper, we get the following system of differential equations:

$$\left.\begin{aligned} L \equiv \frac{\partial \sigma_x}{\partial x} + \frac{\partial \tau_z}{\partial y} + \frac{\partial \tau_y}{\partial z} - \Bigg\{ & \frac{\partial}{\partial x}\left(S_x \cdot \frac{\partial u}{\partial x} + T_z f_z + T_y f_y\right) \\ & + \frac{\partial}{\partial y}\left(S_x f_z + T_z \cdot \frac{\partial v}{\partial y} + T_y f_x\right) + \frac{\partial}{\partial z}\left(S_x f_y + T_z f_x + T_y \cdot \frac{\partial w}{\partial z}\right)\Bigg\} \\ & + T_y \cdot \frac{\partial \omega_y}{\partial x} + T_x \cdot \frac{\partial \omega_y}{\partial y} + S_z \cdot \frac{\partial \omega_y}{\partial z} - \left\{T_z \cdot \frac{\partial \omega_z}{\partial x} + S_y \cdot \frac{\partial \omega_z}{\partial y} + T_x \cdot \frac{\partial \omega_z}{\partial z}\right\} \\ & \qquad + Y \cdot \omega_z - Z \cdot \omega_y = 0. \qquad \textit{cycl.} \end{aligned}\right\} . \quad (20)$$

They govern the transition from an arbitrary state of stress to a state differing from it by an infinitely small amount, when we start from the elastic law introduced in § 3.

The equations:

$$\triangle u + \frac{m}{m-2} \cdot \frac{\partial}{\partial x}\left(\frac{\partial u}{dx} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right) = 0 \quad \textit{cycl.}$$

which are valid when the original state is free from stress, are included in the system (20) as a special case.

Mathematics. — *Ueber unitäre Geometrie.* Von J. A. SCHOUTEN. (Communicated by Prof. W. VAN DER WOUDE).

(Communicated at the meeting of April 27, 1929).

In einer vorigen Mitteilung habe ich gemeinschaftlich mit Herrn D. VAN DANTZIG [1]) gezeigt, dasz ein Hermitescher Tensor n-ten Ranges in einer X_n, der einer bestimmten Differentialgleichung genügt, eine lineare integrable Uebertragung erzeugt, die sich im speziellen Falle, dasz der Tensor im Reellen reell ist, mit der von EINSTEIN verwendeten Weitzenböckschen deckt. Es soll nun darüber hinaus gezeigt werden, dasz *jeder* Hermitesche Tensor n-ten Ranges eine lineare, im allgemeinen nicht integrable Uebertragung erzeugt, und es sollen einige Sätze über die Krümmungstheorie in einer solchen "unitären" Geometrie abgeleitet werden.

1. $\overset{\nu}{x}$ seien die n Koordinaten der X_n, $\overset{N}{x}$ ihre Konjugierten; die kleinen bez. groszen griechischen Buchstaben durchlaufen alle Zeichen der Reihe $a_1, \ldots, a_n$ bez. $\bar{a}_1, \ldots, \bar{a}_n$. Die transformierten Koordinaten seien $\overset{k}{x}, \overset{K}{x}$, wo $h, \ldots, m$ bez. $H, \ldots, M$ die Zeichenreihe $1, \ldots, n$ bez. $\bar{1}, \ldots, \bar{n}$ durchlaufen. Es seien nur analytische, im betrachteten Gebiet reguläre, Transformationen der Koordinaten zugelassen. Für die Definition von Gröszen erster und zweiter Art, Hermitescher Gröszen, Hermitescher Tensoren und analytischer Gröszen sei auf die vorige Mitteilung hingewiesen. Von jeder Grösze setzen wir ausdrücklich voraus, dasz ihre Bestimmungszahlen im betrachteten Gebiet wenigstens reguläre analytische Funktionen der $2n$ Variablen $\overset{\nu}{x}, \overset{N}{x}$ sind. Bei partiellen Ableitungen sind stets diese $2n$ Variablen zu berücksichtigen. Es ist also z. B.

$$\partial_M v^\nu = 0 \quad \text{bez.} \quad \partial_\mu v^N = 0 \; . \; . \; . \; . \; . \; . \; . \; . \qquad (1)$$

die notwendige und hinreichende Bedinging dafür, dasz v^ν bez. v^N analytisch sind.

2. Deuten wir die reellen und durch i dividierten imaginären Teile $\overset{\nu_r}{x}$ und $\overset{\nu_i}{x}$ der Koordinaten:

$$\overset{\nu}{x} = \overset{\nu_r}{x} + i\,\overset{\nu_i}{x} \; ; \quad \overset{N}{x} = \overset{\nu_r}{x} - i\,\overset{\nu_i}{x} \quad . \; . \; . \; . \; . \; . \qquad (2)$$

als Koordinaten einer X_{2n}, so entsprechen sich die reellen Punkte dieser X_{2n} und die komplexen Punkte der X_n eineindeutig. Dagegen bilden sich die in diesen Koordinaten nichtreellen Punkte der X_{2n} nicht auf die X_n ab. Auch $\overset{\nu}{x}$ und $\overset{N}{x}$ lassen sich als Koordinaten der X_{2n} verwenden. Die Gleichungssysteme $\overset{N}{x} =$ konst. und $\overset{\nu}{x} =$ konst. bestimmen in der X_{2n} zwei Systeme von ∞^n in $\overset{\nu_r}{x}$ und $\overset{\nu_i}{x}$ nicht reellen X_n, deren Lage bei Koordinatentransformationen invariant is. Wir wollen diese X_n die *isotropen X_n erster bez. zweiter Art* nennen. Jede isotrope X_n der einen Art wird vermöge der isotropen X_n der anderen Art in eineindeutiger Weise auf jede isotrope X_n der erstgenannten Art abgebildet. Analytisch wird diese Abbildung festgelegt, und zwar unabhängig von der Wahl des Koordinatensystems, durch Gleichsetzen der Werte von $\overset{\nu}{x}$ bez. $\overset{N}{x}$. Infolge der Abbildung besteht eine *Pseudoäquipollenz* zwischen den ∞^n Linienelementen der X_{2n}, deren Anfangspunkte auf einer bestimmten isotropen X_n erster bez. zweiter Art liegen und die auszerdem in einer isotropen X_n zweiter bez. erster Art enthalten sind. Analytisch wird diese Pseudoäquipollenz festgelegt durch Gleichsetzen der Werte von dx^ν bez. dx^N. Jeder kontravariante Vektor in einem Punkte der X_{2n} hat zwei eindeutig bestimmte Komponenten, die Projektionen auf die durch den Punkt gehenden isotropen X_n, wobei stets die andere isotrope X_n die n-Richtung der Projektion festlegt. Ein kontravarianter Vektor v^ν der X_n und sein Konjugierter v^N bilden in der X_{2n} zusammen einen einzigen Vektor mit den $2n$ Bestimmungszahlen v^ν, v^N und seine beiden Komponenten sind die Vektoren der X_{2n} mit den Bestimmungszahlen $v^\nu, 0$ und $0, v^N$. Ebenso bilden eine Hermitesche Grösze z. B. $P_{\mu\lambda}^{\cdot\cdot N}$ und ihre Konjugierte $P_{M\Lambda}^{\cdot\cdot\nu}$ in X_{2n} eine Grösze dritten Grades, von deren Bestimmungszahlen $6n^3$ gleich Null sind, während die übrigen $2n^3$ den $P_{\mu\lambda}^{\cdot\cdot N}$ und $P_{M\Lambda}^{\cdot\cdot\nu}$ gleich sind. Lassen wir die gothischen Indizes $\mathfrak{a}, \mathfrak{b}, \ldots$ alle die $2n$ Zeichen $a_1, \ldots, a_n, \bar{a}_1, \ldots, \bar{a}_n$ durchlaufen, so läszt sich für diese Gröszen schreiben $v^{\mathfrak{c}}$ und $P_{\mathfrak{ab}}^{\cdot\cdot\mathfrak{c}}$. Eine analytische Grösze v^ν ist dadurch gekennzeichnet, dasz die v^ν bez. v^N unabhängig von den $\overset{N}{x}$ bez. $\overset{\nu}{x}$ sind und dies ist gleichbedeutend damit, dasz das Feld $v^\nu, 0$ bez. $0, v^N$ bei der Abbildung der isotropen X_n erster bez. zweiter Art in sich übergeht.

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[1]) Ueber die Differential-geometrie einer Hermiteschen Differentialform und ihre Beziehungen zu den Feldgleichungen des Physik, Proc. Kon. Akad. van Wet. **32** (1929) 60—64.

3. In der X_n soll jetzt eine lineare Uebertragung festgelegt werden, die den formalen Gesetzen in bezug auf Addition und Multiplikation genügt. Die allgemeinste Form einer solchen Uebertragung ist

$$\left.\begin{aligned} \delta v^\nu &= dv^\nu + \Gamma_{\lambda\mu}^{\nu} v^\lambda dx^\mu + \Gamma_{\lambda M}^{\nu} v^\lambda dx^M + \Gamma_{\Lambda\mu}^{\nu} v^\Lambda dx^\mu + \Gamma_{\Lambda M}^{\nu} v^\Lambda dx^M \\ \delta v^N &= dv^N + \Gamma_{\Lambda M}^{N} v^\Lambda dx^M + \Gamma_{\Lambda\mu}^{N} v^\Lambda dx^\mu + \Gamma_{\lambda M}^{N} v^\lambda dx^M + \Gamma_{\lambda\mu}^{N} v^\lambda dx^\mu \end{aligned}\right\} . \quad (3)$$

In der X_{2n} ist dies also eine gewöhnliche lineare Uebertragung. Wir stellen nun die folgenden von der Wahl der Koordinaten unabhängigen Forderungen auf.

1. Jede isotrope X_n erster oder zweiter Art soll geodätisch sein, d.h. in jedem Punkte soll ihre n-Richtung bei jeder von diesem Punkte ausgehenden Verschiebung in einer in der X_n enthaltenen Richtung in sich übergehen.

2. Die n-Richtung einer isotropen X_n erster bez. zweiter Art soll auch bei einer *beliebigen* Verschiebung in eine n-Richtung derselben Art übergehen. Daraus geht hervor, dasz eine X_n erster bez. zweiter Art bei Verschiebung ihrer Punkte über pseudoäquipollente Strecken $0, dx^N$ bez. $dx^\nu, 0$ in eine X_n derselben Art übergeht. Die X_n erster bez. zweiter Art sind also pseudoparallel.

3. Bei der unter 2. erwähnten Verschiebung der Punkte einer isotropen X_n erster bez. zweiter Art über pseudoäquipollente Strecken $0, dx^N$ bez. $dx^\nu, 0$ soll die so entstehende Abbildung zwischen zwei benachbarten X_n derselben Art mit der durch die X_n zweiter bez. erster Art erzeugten Abbildung zusammenfallen.

4. Die kovarianten Differentiale zweier konjugierter Gröszen sollen selbst konjugiert sein.

Aus der ersten Forderung geht hervor:

$$\Gamma^{\nu}_{\Lambda M} = \Gamma^{N}_{\lambda\mu} = 0 \quad \ldots\ldots\ldots \quad (4)$$

Aus der zweiten Forderung geht hervor:

$$\Gamma^{\nu}_{\Lambda\mu} = \Gamma^{N}_{\lambda M} = 0 \quad \ldots\ldots\ldots \quad (5)$$

Aus der dritten Forderung folgt:

$$\Gamma^{\nu}_{\lambda M} = \Gamma^{N}_{\Lambda\mu} = 0 \,.\quad \ldots\ldots\ldots \quad (6)$$

Aus der vierten Forderung folgt, dasz $\Gamma^{\nu}_{\lambda\mu}$ und $\Gamma^{N}_{\Lambda M}$ konjugiert komplex sind:

$$\Gamma^{N}_{\Lambda M} = \overline{\Gamma}^{\nu}_{\lambda\mu} \quad \ldots\ldots\ldots \quad (7)$$

Die Uebertragung bekommt also die Form

$$\left.\begin{aligned} \delta v^\nu &= \partial_\mu v^\nu \, dx^\mu + \partial_M v^\nu \, dx^M + \Gamma^{\nu}_{\lambda\mu} v^\lambda \, dx^\mu \\ \delta v^N &= \partial_M v^N dx^M + \partial_\mu v^N dx^\mu + \Gamma^{N}_{\Lambda M} v^\Lambda dx^M \end{aligned}\right\} \quad \ldots\ldots \quad (8)$$

die für den Fall, dasz v^ν analytisch ist, übergeht in

$$\left.\begin{aligned} \delta v^\nu &= \partial_\mu v^\nu \, dx^\mu + \Gamma^{\nu}_{\lambda\mu} v^\lambda \, dx^\mu \\ \delta v^N &= \partial_M v^N dx^M + \Gamma^{N}_{\Lambda M} v^\Lambda dx^M \end{aligned}\right\} \quad \ldots\ldots \quad (9)$$

Für analytische Gröszen gelten also infolge unserer Annahmen die gewöhnlichen Gleichungen und im Falle, dasz $\Gamma^{\nu}_{\lambda\mu}$ analytisch in $\overset{\nu}{x}$ ist, ist sogar das kovariante Differential einer analytischen Grösze wiederum analytisch. Von diesem Spezialfalle sehen wir hier im Gegensatz zur oben zitierten Mitteilung im Allgemeinen ab. Die Gleichungen

$$\left.\begin{aligned} \nabla_{\mu} v^{\nu} &= \partial_{\mu} v^{\nu} + \Gamma^{\nu}_{\lambda\mu} v^{\lambda} \\ \nabla_{M} v^{\nu} &= \partial_{M} v^{\nu} \\ \nabla_{\mu} v^{N} &= \partial_{\mu} v^{N} \\ \nabla_{M} v^{N} &= \partial_{M} v^{N} + \Gamma^{N}_{\Lambda M} v^{\Lambda} \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (10)$$

definieren vier paarweise konjugierte Gröszen, die kovarianten Differentialquotienten von v^{ν} und v^{N}, die sich als Komponenten des kovarianten Differentialquotienten von $v^{\mathfrak{c}}$

$$\nabla_{\mathfrak{b}} v^{\mathfrak{c}} = \partial_{\mathfrak{b}} v^{\mathfrak{c}} + \Gamma^{\mathfrak{c}}_{\mathfrak{a}\mathfrak{b}} v^{\mathfrak{a}} \quad \ldots\ldots\ldots \quad (11)$$

in X_{2n} auffassen lassen.

4. In der X_n sei jetzt ein kovarianter Hermitescher Tensor (Hermitesch-symmetrische Grösze) zweiten Grades n-ten Ranges

$$g_{\lambda M} = \overline{g_{\Lambda\mu}} = g_{M\lambda} \quad \ldots\ldots\ldots \quad (12)$$

eingeführt. Die X_n, die in solcher Weise eine Hermitesche Maszbestimmung bekommen hat, soll U_n heiszen. Wir behaupten, dasz durch die zusätzliche Forderung, dasz das kovariante Differential von $g_{\lambda M}$ verschwinden soll, eine Uebertragung vollständig festgelegt ist. In der Tat ergibt die Gleichung

$$0 = \delta g_{\lambda M} = \underset{\textit{konj.}^{1)}}{\partial_{\omega} g_{\lambda M}} dx^{\omega} + \partial_{\Omega} g_{\lambda M} dx^{\Omega} + \Gamma^{\nu}_{\lambda\omega} g_{\nu M} dx^{\omega} + \Gamma^{N}_{M\Omega} g_{\lambda N} dx^{\Omega} \quad (13)$$

unmittelbar:

$$\left.\begin{aligned} \Gamma^{\nu}_{\lambda\omega} &= g^{M\nu} \partial_{\omega} g_{\lambda M} \\ \Gamma^{N}_{\Lambda\Omega} &= g^{N\mu} \partial_{\Omega} g_{\mu\Lambda} \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (14)$$

und diese Gleichungen sind verträglich wegen der in (12) vorausgesetzten Hermiteschen Symmetrie.

Man berechnet leicht, dasz die Krümmungsgrösze der Uebertragung

$$R_{\mathfrak{d}\mathfrak{b}\mathfrak{a}}^{\cdot\cdot\cdot\,\mathfrak{c}} = 2\,\partial_{[\mathfrak{d}}\, \Gamma^{\mathfrak{c}}_{|\mathfrak{a}|\mathfrak{b}]} - 2\,\Gamma^{\mathfrak{c}}_{\mathfrak{e}[\mathfrak{d}}\, \Gamma^{\mathfrak{e}}_{|\mathfrak{a}|\mathfrak{b}]} \quad \ldots\ldots \quad (15)$$

nur die folgenden nicht verschwindenden Bestimmungszahlen hat:

$$\left.\begin{aligned} R_{\Omega\dot{\mu}\dot{\lambda}}{}^{\nu} &\overset{*}{=} - R_{\dot{\mu}\dot{\Omega}\lambda}{}^{\nu} \overset{*}{=} - \partial_{\Omega} \Gamma^{\nu}_{\lambda\mu} \\ R_{\dot{\omega}\dot{M}\lambda}{}^{N} &\overset{*}{=} - R_{\dot{M}\dot{\omega}\Lambda}{}^{N} \overset{*}{=} - \partial_{\omega} \Gamma^{N}_{\Lambda M} \end{aligned}\right\} \textit{konj.}^{\,2)} \quad \ldots \quad (16)$$

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1) „konj." soll stets bedeuten, dasz auch die konjugierte Gleichung ausgeschrieben zu denken ist.

2) Wir verwenden das Zeichen $\overset{*}{=}$ in Gleichungen, die Grössen enthalten, überall dort, wo nur numerische Gleichheit in bezug auf das gerade gewählte Bezugssystem besteht aber links und rechts Ausdrücke auftreten die sich in verschiedener Weize transformieren. Eine Gleichung mit $\overset{*}{=}$ darf also nicht kovariant differenziert werden.

Verschwinden auch diese, so wird die Uebertragung integrabel und es werden gleichzeitig die $\Gamma_{\lambda\mu}^{\nu}$ analytisch in $\overset{\nu}{x}$. Dies ist der in der oben zitierten Mitteilung behandelte Fall. Auszer der aus (16) unmittelbar folgenden ersten Identität[1], gilt auch die zweite[2], die hier die Form

$$R_{\dot{\Omega}\dot{\mu}\dot{\lambda}}{}^{\nu} - \underset{konj.}{R_{\dot{\Omega}\dot{\lambda}\dot{\mu}}{}^{\nu}} = 2\,\partial_{\Omega} S_{\dot{\lambda}\dot{\mu}}{}^{\nu} = 2\nabla_{\Omega} S_{\dot{\lambda}\dot{\mu}}{}^{\nu} \quad . \; . \; . \; . \quad (17)$$

annimmt. Werden die Indizes ν und N mit Hilfe von $g_{\lambda M}$ heruntergezogen, so gilt auch die dritte Identität[2])

$$R_{\Omega\mu\lambda N} \underset{konj.}{=} - R_{\Omega\mu N\lambda} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (18)$$

Aus (17) und (18) folgt schlieszlich die vierte Identität[3], die hier die Form annimmt

$$R_{\Omega\mu\lambda N} - \underset{konj.}{R_{\lambda N\Omega\mu}} = 2\, \nabla_{\lambda}\, S_{\Omega N\mu} - 2\, \nabla_{\Omega}\, S_{\lambda\mu N} \quad . \; . \; . \quad (19)$$

Auch die Bianchische Identität[4] gilt und nimmt die Form an

$$\nabla_{[\mu} R_{\dot{\xi}]\dot{\Omega}\dot{\lambda}}{}^{\nu} = S_{\dot{\mu}\dot{\xi}}{}^{\alpha} R_{\dot{\alpha}\dot{\Omega}\dot{\lambda}}{}^{\nu} \; ; \nabla_{[\mu} R_{\dot{\xi}]\dot{\Omega}\dot{\Lambda}}{}^{N} = S_{\dot{\mu}\dot{\xi}}{}^{\alpha} R_{\dot{\alpha}\dot{\Omega}\dot{\Lambda}}{}^{N} \Big\} \; konj. \quad . \; . \quad (20)$$

Durch die Maszbestimmung

$$ds^2 = 2\, dx^{\lambda}\, dx^{M}\, g_{\lambda M} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (21)$$

wird in der X_{2n} ein gewöhnlicher Fundamentaltensor

$$G_{\lambda M} = g_{\lambda M} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (22)$$

festgelegt. Die zu diesem Tensor gehörige Riemannsche Geometrie hat die Parameter

$$\overset{R}{\Gamma}{}_{\lambda\mu}^{\nu} = \Gamma_{(\lambda\mu)}^{\nu} \quad ; \quad \underset{konj.}{\overset{R}{\Gamma}{}_{\lambda M}^{\nu}} = \overset{R}{\Gamma}{}_{M\lambda}^{\nu} = g^{\nu A}\, g_{\lambda\Gamma}\, S_{\dot{A}\dot{M}}{}^{\Gamma} \quad ; \quad \overset{R}{\Gamma}{}_{\lambda\mu}^{N} = 0 \quad . \quad (23)$$

und daraus geht hervor, dasz die zugehörige Uebertragung den im § 3 aufgestellten Forderungen 1 und 4 genügt. Die isotropen X_n sind also auch in bezug auf diese Uebertragungen geodätisch, sie sind aber nicht mehr geodätisch parallel, und von einer gegenseitigen Abbildung bei pseudoäquipollenter Verschiebung kann also gar nicht die Rede sein.

5. Ist s die mittels (21) auf einer Kurve in U_n definierte Bogenlänge, so ist $i^{\nu} = dx^{\nu}/ds$ der unitäre Einheitsvektor in der Tangente und

$$u^{\nu} = i^{\mu}\, \nabla_{\mu}\, i^{\nu} + i^{M}\, \nabla_{M}\, i^{\nu} = \frac{d^2 x^{\nu}}{ds^2} + \Gamma_{\lambda\mu}^{\nu} \frac{dx^{\lambda}}{ds} \frac{dx^{\mu}}{ds} \quad . \; . \quad (24)$$

der erste Krümmungsvektor, der unitär orthogonal zu i^{ν} ist.

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[1] R. K. (Der Ricci-Kalkül, Springer 1924) S. 87.

[2] R. K. S. 88.

[3] R. K. S. 89.

[4] R. K. S. 90.

Sein Verschwinden ist das Kriterium für eine geodätische Linie. Geht $g_{\lambda M}$ über in $\sigma g_{\lambda M}$ mit reellem σ und ist die neue Bogenlänge $'s$, so ist $d's = \sigma^{1/2} ds$ und aus (14) ergiebt sich

$$'\Gamma^{\nu}_{\lambda\mu} = \Gamma^{\nu}_{\lambda\mu} + A^{\nu}_{\lambda}\, \partial_{\mu} \log \sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

sodasz

$$'u^{\nu} = \sigma^{-1} u^{\nu} + {}^{1}/_{2}\, \sigma^{-1} i^{\nu} (i^{\mu}\, \partial_{\mu} \log \sigma - i^{M}\, \partial_{M} \log \sigma) \quad . \quad . \quad . \quad (26)$$

Selbstverständlich ist auch $'u^{\nu}$ unitär orthogonal zu i^{ν} und dies kommt dadurch zu stande, dasz $i^{\nu} \sqrt{-1}$ unitär orthogonal zu i^{ν} ist.

6. In der U_n sei eine X_m gegeben mittels der Parametergleichungen

$$\overset{\nu}{x} = \overset{\nu}{x}(\overset{1}{y}, \dots, \overset{m}{y}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

mit m komplexen Parametern $\overset{a}{y}$, wo $a, b, \dots, g$ die Zeichen $1, \dots, m$ durchlaufen. Die konjugierten Werte seien durch $\overset{A}{y}$, $A, \dots, G = \overline{1}, \dots, \overline{m}$ angedeutet. Die in diesen Gleichungen auftretenden Funktionen seien alle analytisch. Dann ist jede isotrope X_m der X_{2m} in einer isotropen X_n der X_{2n} enthalten. Wir bilden zunächst die Gröszen

$$B^{\nu}_{a} = \partial_{a}\, x^{\nu}\, ; \; B^{N}_{A} = \partial_{A}\, x^{N}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

aus diesen Gröszen und $g_{\lambda M}$ den Fundamentaltensor g'_{aB} der X^{m}

$$g'_{aB} = B^{\lambda M}_{aB}\, g_{\lambda M}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

und mittels g'_{aB}

$$B^{c}_{\lambda} = g'^{Bc}\, B^{N}_{B}\, g_{\lambda N}\, ; \; B^{C}_{\Lambda} = g'^{bC}\, B^{\nu}_{b}\, g_{\Lambda\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

und

$$B^{c}_{a} = B^{\beta}_{a}\, B^{c}_{\beta} = \begin{cases} 1, & a = c \\ 0, & a \neq c \end{cases}; \; B^{\nu}_{\lambda} = B^{\nu}_{b}\, B^{b}_{\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Die $B^{\nu}_{a}, B^{c}_{\lambda}, B^{c}_{a}$, und B^{ν}_{λ} fassen wir alle als verschiedene Arten von Bestimmungszahlen des Einheitsaffinors B der X_m auf. Dies ist alles genau wie bei einer X_m in V_n mit dem einzigen Unterschiede, dasz statt eines gewöhnlichen ein Hermitescher Fundamentaltensor auftritt. Es ist zu beachten, dasz zwar die B^{ν}_{a}, im allgemeinen aber nicht mehr die B^{c}_{λ} analytische Funktionen der $\overset{\nu}{x}$ sind.

Mittels B^{ν}_{λ} läszt sich zu jedem in einem Punkte der X_m definierten Vektor v^{ν} bez. w_{λ} der U_n die Projektion $B^{\nu}_{\lambda} v^{\lambda}$ bez. $B^{\nu}_{\lambda} w_{\nu}$ auf X_m bilden. Die in X_m induzierte Uebertragung wird erhalten aus der Forderung, dasz das kovariante Differential die Projektion des kovarianten Differentials in der X_n sein soll

$$\delta' v^{\nu} = B^{\nu}_{\lambda}\, \delta v^{\lambda} = B^{\nu}_{\lambda}\, dv^{\lambda} + B^{\nu}_{\alpha}\, \Gamma^{\alpha}_{\lambda\mu}\, v^{\lambda}\, dx^{\mu} \quad . \quad . \quad . \quad . \quad . \quad (32)$$

oder in bezug auf die Variablen $y^{\cdot}$:

$$\left.\begin{aligned} \delta' v^c &= B^c_\lambda \, \delta v^\lambda = B^c_\lambda dv^\lambda + B^c_\alpha \, \Gamma^\alpha_{\lambda\mu} \, v^\lambda \;\, dx^\mu \\ &= dv^c - v^a \, dy^b \, B^\lambda_a \, \partial_b \, B^c_\lambda + B^{c\lambda\mu}_{\alpha ab} \, \Gamma^\alpha_{\lambda\mu} \, v^a \, dy^b \end{aligned}\right\} \quad . \quad . \quad (33)$$

woraus für die Parameter Γ'^c_{ab} der induzierten Uebertragung folgt:

$$\Gamma'^c_{ab} = B^{c\lambda\mu}_{\nu ab} \, \Gamma^\nu_{\lambda\mu} + B^c_\lambda \, \partial_b \, B^\lambda_a \, ; \; konj. \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Wir stellen zunächst fest, dasz die induzierte Uebertragung zum Fundamentaltensor g'_{aB} gehört. In der Tat ist:

$$\delta' \, g'_{aB} = B^{\lambda M}_{aB} \, \delta g_{\lambda M} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Ferner folgt aus (34), dasz die für die Asymmetrie der induzierten Uebertragung charakteristische Grösze

$$S'^{\cdot\cdot c}_{ab} = \Gamma'^c_{[ab]} = B^{c\lambda\mu}_{\nu ab} \, S^{\cdot\cdot\nu}_{\lambda\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

die X_m-Komponente von $S^{\cdot\cdot\nu}_{\lambda\mu}$ ist.

Aus der Definition der induzierten Uebertragung ergiebt sich für ein Feld v^ν, das in der X_m liegt:

$$\left.\begin{aligned} B^\beta_\mu \nabla_\beta \, v^\nu &= B^\beta_\mu \nabla'_\beta \, v^\nu + v^\lambda \, H^{\cdot\cdot\nu}_{\lambda\mu} \\ B^B_M \nabla_B \, v^\nu &= B^B_M \nabla'_\beta \, v^\nu \end{aligned}\right\} \; konj. \quad . \quad . \quad . \quad . \quad . \quad (37)$$

wo

$$H^{\cdot\cdot\nu}_{\mu\lambda} = B^{\beta\alpha}_{\mu\lambda} \nabla_\beta \, B^\nu_\alpha \, ; \; konj. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

$H^{\cdot\cdot\nu}_{\mu\lambda}$ und $H^{\cdot\cdot N}_{M\Lambda}$ lassen sich als Komponenten des ersten Krümmungsaffinors $H^{\cdot\cdot c}_{\mathfrak{ba}}$ der X_{2m} in X_{2n} auffassen. Der daneben existierende zweite Krümmungsaffinor mit den Komponenten:

$$L^{\cdot\nu}_{M\cdot\lambda} = B^{B\nu}_{M\alpha} \nabla_B B^\alpha_\lambda \; ; \; konj. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

tritt auf bei der differentiation eines kovarianten in der X_m liegenden Vektorfeldes:

$$\left.\begin{aligned} B^\beta_\mu \nabla_\beta \, w_\lambda &= B^\beta_\mu \nabla'_\beta \, w_\lambda \\ B^B_M \nabla_B \, w_\lambda &= B^B_M \nabla'_B \, w_\lambda + w_\nu \, L^{\cdot\nu}_{M\cdot\lambda} \end{aligned}\right\} \; konj. \quad . \quad . \quad . \quad (40)$$

Für die Bestimmungszahlen $H^{\cdot\cdot\nu}_{ba}$ gilt:

$$H^{\cdot\cdot\nu}_{ba} = \partial_b \, B^\nu_a - \Gamma'^c_{ab} \, B^\nu_c = \Gamma^\nu_{\lambda\mu} \, B^{\lambda\mu}_{ab} \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

Die Gaussische Gleichung nimmt folgende Gestalt an

$$B^{\Delta\beta\alpha\Gamma}_{\Omega\mu\lambda N} \, R_{\Delta\beta\alpha\Gamma} = R'_{\Omega\mu\lambda N} + H_{\lambda\mu A} \, H_{\Omega N\beta} \, g^{A\beta} \, ; \; konj. \quad . \quad . \quad . \quad (42)$$

Bei Anwendung der erhaltenen Formeln auf den Fall $m = 1$ ergibt sich, wenn wir einfachshalber y statt y^1 und $\bar{y}$ statt y^1 schreiben

$$\left.\begin{aligned}
B^{\nu}_{1} &= \frac{dx^{\nu}}{dy} \quad ; \quad g'_{1\bar{1}} = \frac{ds}{dy}\frac{\overline{ds}}{d\bar{y}} = \left|\frac{ds}{dy}\right|^2 \\
B^{1}_{\lambda} &= g_{\lambda N}\frac{dy}{ds}\frac{dx^{N}}{ds} \\
\Gamma'^{1}_{11} &= \frac{dy}{ds}\frac{d\bar{y}}{ds}\frac{d}{dy}\left(\frac{ds}{dy}\frac{\overline{ds}}{d\bar{y}}\right) = 2\frac{d}{dy}\log\left|\frac{ds}{dy}\right| \\
H_{11}{}^{\nu} &= \frac{d^2x^{\nu}}{dy^2} - 2\frac{dx^{\nu}}{dy}\frac{d}{dy}\log\left|\frac{ds}{dy}\right| + \Gamma^{\nu}_{\lambda\mu}\frac{dx^{\lambda}}{dy}\frac{dx^{\mu}}{dy} = \\
&= g^{A\nu}\frac{d}{dy}\left(g_{\lambda A}\frac{dx^{\lambda}}{dy}\right) - \frac{dx^{\nu}}{dy}\frac{d}{dy}\log\left|\frac{ds}{dy}\right|
\end{aligned}\right\} \qquad (43)$$

7. Die reellen Punkte der U_n bilden sich in der X_{2n} ab auf die X_n

$$\overset{\nu_i}{x} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (44)$$

Beim Uebergang von den Koordinaten $\overset{\nu}{x}, \overset{N}{x}$ zu $\overset{\nu_0}{x}, \overset{\nu_i}{x}$ transformieren sich die Bestimmungszahlen der Gröszen der X_{2n} mit Hilfe der folgenden Bestimmungszahlen von A:

$$\left.\begin{aligned}
A^{\nu}_{\lambda_r} &\overset{*}{=} \frac{1}{i}A^{\nu}_{\lambda_i} \overset{*}{=} 2A^{\nu_r}_{\lambda} \overset{*}{=} 2A^{\nu_r}_{\Lambda} \overset{*}{=} \varepsilon^{\nu}_{\lambda} \\
A^{N}_{\lambda_r} &\overset{*}{=} -\frac{1}{i}A^{N}_{\lambda_i} \overset{*}{=} 2A^{\nu_i}_{\lambda} \overset{*}{=} -2A^{\nu_i}_{\Lambda} \overset{*}{=} \varepsilon^{\nu}_{\lambda}
\end{aligned}\right\}{}^{1)} \quad . \quad . \quad . \qquad (45)$$

infolgedessen ist

$$\left.\begin{aligned}
G_{\lambda_r\mu_r} &\overset{*}{=} G_{\lambda_i\mu_i} \overset{*}{=} G_{\lambda M} + G_{\Lambda\mu} \\
G_{\lambda_r\mu_i} &\overset{*}{=} G_{\mu_i\lambda_r} \overset{*}{=} -G_{\lambda M} + G_{\lambda M}
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \qquad (46)$$

und es gilt also der Satz:

Die Parameterlinien von $\overset{\nu_i}{x}$ *sind dann und nur dann senkrecht zur* X_n, *die das Reelle der* U_n *abbildet, wenn der Fundamentaltensor* $g_{\lambda M}$ *im Reellen der* U_n *reell ist.*

Wir spannen jetzt die X_n der reellen Punkte der U_n ein mit Hilfe der Parameterlinien von $\overset{\nu_i}{x}$. Dann ergiebt sich

$$B^{\nu}_{\lambda} \overset{*}{=} B^{N}_{\lambda} \overset{*}{=} B^{\nu}_{\Lambda} \overset{*}{=} B^{N}_{\Lambda} \overset{*}{=} {}^1\!/_2\, \varepsilon^{N}_{\Lambda} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (47)$$

und

$$\left.\begin{aligned}
&H_{\mu\lambda}{}^{\cdot\cdot\nu} \overset{*}{=} H_{M\lambda}{}^{\cdot\cdot\nu} \overset{*}{=} H_{\mu\Lambda}{}^{\cdot\cdot\nu} \overset{*}{=} H_{M\Lambda}{}^{\cdot\cdot\nu} \overset{*}{=} -H_{\mu\lambda}{}^{\cdot\cdot N} \overset{*}{=} -H_{M\lambda}{}^{\cdot\cdot N} \overset{*}{=} -H_{\mu\Lambda}{}^{\cdot\cdot N} \overset{*}{=} \\
&\qquad \overset{*}{=} H_{M\Lambda}{}^{\cdot\cdot N} \overset{*}{=} \tfrac{1}{8}\left(\Gamma^{\nu}_{\lambda\mu} - \Gamma^{N}_{\Lambda M}\right).
\end{aligned}\right\} \qquad (48)$$

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1) Das Kroneckersche Symbol $\varepsilon^{\nu}_{\lambda}$ sowie auch $\varepsilon^{N}_{\Lambda}$ bedeuted 1 oder 0 je nachdem für die Indices gleiche oder ungleiche Zeichen eingesetzt werden.

Ist nun $g_{\lambda M}$ im Reellen der U_n reell, so ist

$$\left.\begin{aligned} \Gamma^{\nu}_{\lambda\mu} &= g^{A\nu}\partial_{\mu}\, g_{\lambda M} = g^{A\nu} A^{\beta_r}_{\mu}\, \partial_{\beta_r} g_{\lambda M} + g^{A\nu} A^{\beta_i}_{\mu}\, \partial_{\beta_i} g_{\lambda M} \\ \Gamma^{N}_{AM} &= g^{\alpha N}\partial_{M} g_{A\alpha} = g^{\alpha N} A^{\beta_r}_{M}\, \partial_{\beta_r} g_{A\alpha} + g^{\alpha N} A^{\beta_i}_{M}\, \partial_{\beta_i} g_{A\alpha} \end{aligned}\right\} \quad . \quad . \quad (49)$$

Da aber das erste Glied rechts reell ist folgt bei Subtraktion unter Berücksichtigung von (45)

$$\left.\begin{aligned} \Gamma^{\nu}_{\lambda\mu} - \Gamma^{N}_{AM} &= {}^1\!/_2\, \varepsilon^{\beta_i}_{\mu}\, g^{A\nu}\, \partial_{\beta_i} g_{\lambda A} + \tfrac{1}{2}\, \varepsilon^{\beta_i}_{M}\, g^{\alpha N}\, \partial_{\beta_i} g_{A\alpha} = \\ &= {}^1\!/_2\, \varepsilon^{\beta}_{\mu}\, g^{A\nu}\, \partial_{\beta_i} (g_{\lambda M} + g_{A\mu}) \end{aligned}\right\} \quad . \quad . \quad . \quad (50)$$

Nun verschwindet nach Voraussetzung $\partial_{\mu_r}(g_{\lambda M} - g_{A\mu})$. Sind also die $g_{\lambda M}$ nicht nur im Reellen reell sondern auszerdem analytische Funktionen der $\overset{\nu}{x}$, so verschwindet $\partial_{\mu_i}(g_{\lambda M} + g_{A\mu})$ und damit die rechte Seite von (50). Es gilt also der Satz:

Ist der Hermiteschen Fundamentaltensor $g_{\lambda M}$ im Reellen reell und sind auszerdem seine Bestimmungszahlen analytische Funktionen der $\overset{\nu}{x}$, so ist die X_n, die das Reelle der U_n in der X_{2n} abbildet, in dieser X_{2n} geodätisch in Bezug auf die Uebertragung mit den Parametern $\Gamma^{\nu}_{\lambda\mu} = g^{\nu A}\,\partial_{\mu}\, g_{\lambda A}$.

Es ist gerade dieser Fall, der zu der von EINSTEIN verwendeten Fernübertragung führt, wie in der oben zitierten Mitteilung gezeigt wurde.

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[1] Das erweiterte Kroneckersche Symbol ε soll 1 oder 0 bedeuten, je nachdem die beiden Indizes in ihren Zeichenreihen korrespondierende Stellen einnehmen oder nicht. Es ist also z. B.

$$\varepsilon^{N}_{\lambda} = 1 \text{ wenn } \lambda = a_i\,,\ N = \bar{a}_i \text{ und } \varepsilon^{N}_{\lambda} = 0 \text{ wenn } \lambda = a_i\,,\ N = \bar{a}_j\,,\ i \neq j\,.$$

Anatomy. — *The Phylogenetic Development of the Substantia Gelatinosa Rolandi.* Part III [1]). *Mammals, General Résumé, and Conclusions.*

By E. KEENAN, M. B., National University of Ireland. (From the Central Dutch Institute for Brain Research, Amsterdam.) (Communicated by Prof. C. U. ARIËNS KAPPERS.)

(Communicated at the meeting of April 27, 1929).

The examination of the spinal cords of a large number of mammals confirms the view of SANO (1909) that substantia gelatinosa Rolandi is of general occurrence throughout this subdivision of the vertebrates.

The most prominent general feature of the substance is its cap-like form, as it surrounds the extremity of the body of the posterior horn. In its simplest appearance, such as is seen in the thoracic region of the cord of man (cf. also fig. 2), it is folded around the extremity of the body of the horn as a narrow layer, extending downwards on the lateral and medial sides for about equal distances. In more complicated forms it is, in addition, folded on itself, and may extend down along the medial side of the horn, sometimes as far as the median septum as in Simia satyrus, and may even be continuous with the gelatinous substance of the other side. In the elephant, it is arranged in a double cap-like manner so that the posterior horn appears bifurcated at its extremity.

In animals in which the substance is strongly developed, folding on itself frequently occurs. There are many instances of this among the ungulates. A similar condition was observed in Albula vulpes and other teleosts (Part I). Even in man, in the cervical region, the same tendency is manifest, though in a small degree. In the lumbar and sacral regions, where the substance is generally very well developed, folding does not occur to the extent one should expect, but here the posterior horn is very broad, and is occupied almost entirely by a great mass of gelatinous substance.

Figs. 1, 2, 3, and 4 show the relationships in the cervical, thoracic, lumbar, and sacral regions, respectively, of the cord of Hylobates spec.

In the cervical region, the posterior horn is somewhat club-shaped, with a very narrow neck. The swelling of the end of the horn is chiefly due to the accumulation of gelatinous substance. In the thoracic region (fig. 2), the posterior horn is very narrow, and the substantia gelatinosa is greatly reduced in amount. In the lumbar and sacral regions (figs. 3 and 4), a great enlargement of the horn occurs, and with it an increase in the gelatinous substance.

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[1]) Part I. Fishes, These Proc., Vol. **31**. 1928.
Part II. Amphibians, Reptiles, and Birds, These Proc., Vol. **32**. 1929.

A comparison of the various segments of the cord gives the following results: as we pass downwards from the upper cervical region, the

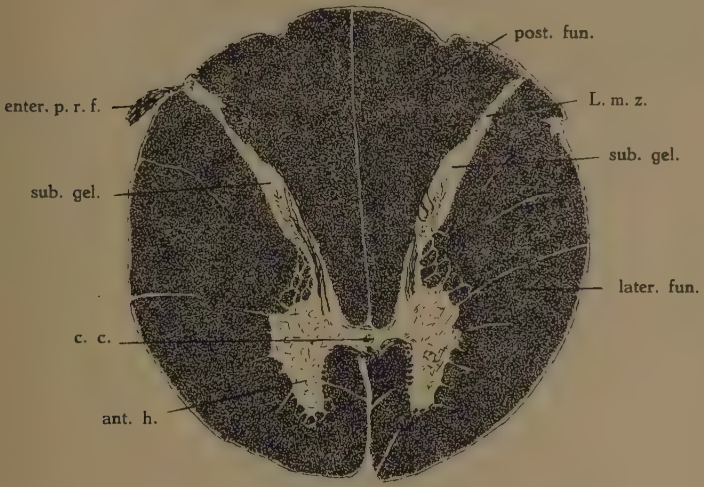

Fig. 1. Transverse section through the 2nd cervical segment of the spinal cord of Hylobates spec. × 12.

ABBREVIATIONS FOR ALL FIGURES.

ant. fun. = anterior funiculus.
ant. h. = anterior horn.
ant. r. f. = anterior root fibres.
b. of p. h. = body of the posterior horn.
c. c. = central canal.
enter. p. r. f. = entering posterior root fibres.
later. fun. = lateral funiculus.
later. h. = lateral horn.
L. m. z. = LISSAUER's marginal zone.
post. fun. = posterior funiculus.
sub. gel. = substantia gelatinosa.

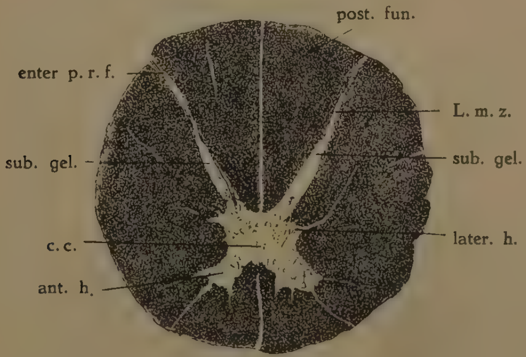

Fig. 2. Transverse section through the 4th thoracic segment of the spinal cord of Hylobates spec. × 12.

gelatinous substance is reduced in amount until the cervical swelling is reached, where it increases again. It is actually better developed here than in the cord higher up. Below this point, it decreases again, and, about the mid-thoracic region, the development reaches its lowest point. Caudal to this, it increases again, and in the lumbosacral swelling it reaches its maximum size. Reference to SANO's tables shows this curve to be general for all the mammals examined by him. Though it is actually increased in the cervical swelling, in most animals there may be a relative decrease, owing to the increased size of all parts of the cord at this level.

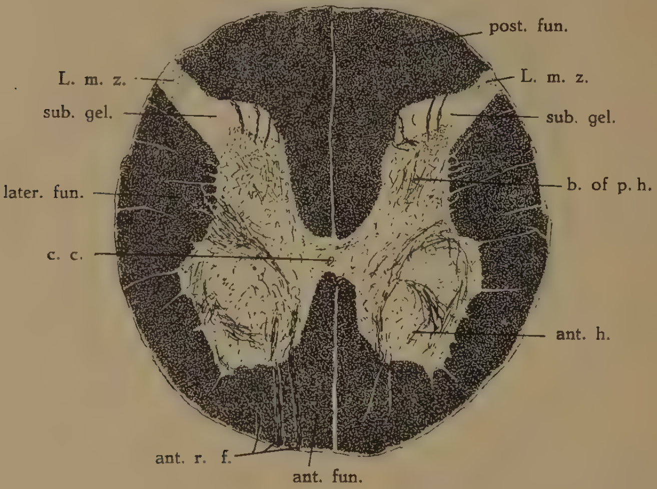

Fig. 3. Transverse section through the 3rd lumbar segment of the spinal cord of Hylobates spec. × 12.

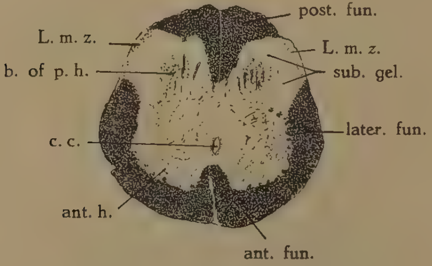

Fig. 4. Transverse section through the 2nd sacral segment of the spinal cord of Hylobates spec. × 12.

Lissauer's zone narrows and deepens as the posterior horn recedes further from the surface. This change, however, is not as well marked here as in Simia satyrus. In the latter, the substantia gelatinosa reaches to within a short distance from the surface in the upper cervical region, whereas in Hylobates, even in the second cervical segment, Lissauer's zone is of considerable depth (fig. 1). In the mid-thoracic region it is a very slender strand, stretching from the bottom of the postero-lateral sulcus to the substantia gelatinosa, and it practically equals in length the posterior horn. As the horn approaches the surface and widens, in the caudal end of the cord, Lissauer's zone also shortens and widens. In the sacral region (fig. 4), it lies as a flattened band on the surface of the cord.

A comparison of the relative development of the substantia gelatinosa in various mammals shows, as in the case of lower vertebrates, no well marked lines of separation based on systematic classification. Animals such as Xantharpya amplexicaudata, Macropus robustus, and Tamandua tetradactyla stand much higher in development than man, Simia satyrus, and Hylobates spec., while Phocaena communis, and Tursio tursiops, are lower in development.

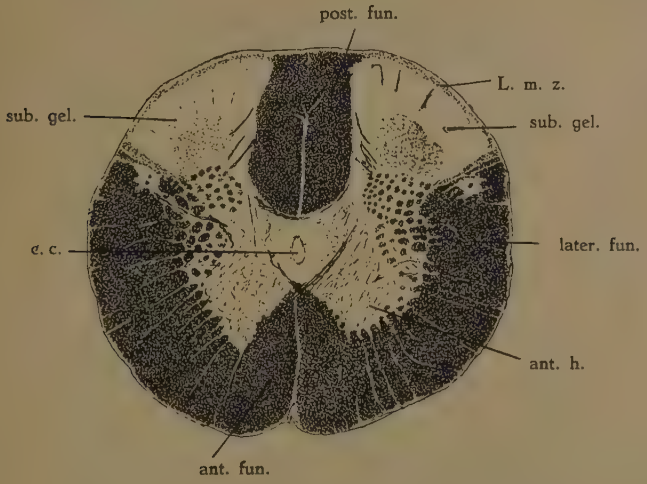

Fig. 5. Transverse section through the upper cervical region of the spinal cord of Xantharpya amplexicaudata × 30.

I can also confirm RANSON's observation in the case of the rat and Guinea pig, that Lissauer's zone by no means varies in relative development with the substantia gelatinosa in different animals. In Xantharpya amplexicaudata, where the gelatinous substance is very well developed, Lissauer's zone is quite small. No marked extension of the zone into the lateral funiculus could be seen in this species which might account for the small size of the apical tract (fig. 5).

General résumé.

A general survey of the substantia gelatinosa throughout the vertebrates brings out some important facts. Firstly, the substance is of universal occurrence down to and including the fishes. That the vertebrates below the fishes, Amphioxus and the cyclostomes, are practically neglected in this study is due to the facts (1) that in these forms all nerve-fibres are unmyelinated and consequently the typical appearance of the substance, even if present, would not be seen in WEIGERT—PAL preparations, and (2) that the cords do not conform, in the arrangement of the gray matter, to those of higher forms. In Amphioxus, horn formation is not indicated, while in the cyclostomes, a lateral wing of gray matter on either side represents the combined anterior and posterior horns (cf. KAPPERS, 1920). While these facts do not exclude the possibility of the substance, or at least of gray matter having similar relations to it, they render its recognition impossible by the method of staining used in this study.

In *fishes*, even among the lowest members, the cord has reached a development which renders possible a recognition of its main parts. The nerve-fibres are myelinated; the gray matter is so arranged that both anterior and posterior horns are recognizable. The anterior horns are better differentiated than the posterior. The posterior horn region may be recognized in two parts, (1), the primitive posterior horns of these animals, which consist of substantia gelatinosa, and are attached centrally to (2), the corpus commune posterius, which lies behind the central canal, and is homologous to the fused bodies of the posterior horns of higher vertebrates. This structure is best seen in sharks (Part I, figs. 1 and 2), though it is also present in most species of teleosts, and is recognizable in amphibians also.

Lissauer's marginal zone of mammals is not present as a separate apical tract, though fine and medium sized fibres are scattered through the gray matter of the horn and on all sides of it. LESZLÉNYI (1912) mentions these fibres in Torpedo marmorata and Carcharias glaucus, though he does not definitely recognize them as a Lissauer's zone.

The posterior funiculi of fishes are very small, and it is doubtful if any of the fibres contained in it reach the medulla oblongata. The fibres are chiefly root fibres which have a relatively short course within the cord, and possibly also association fibres. Posterior funicular nuclei, e.i. nuclei of GOLL and BURDACH, have not been recognized (BROUWER, 1915).

The development of the substantia gelatinosa varies much in fishes, from the enormous development in Albula, where it occupies, in the upper end of the cord, almost half the total area of cross section, to the very small amount in Malapterurus electricus, with all degrees of development in between. Generally speaking, however, *the relation in the amount of the gelatinous substance to that of the corpus commune posterius is very much in favour of the former in fishes.*

In the upper cervical region of the cord, where descending fibres of the fifth and other cranial nerves are present, the amount is far in excess of that lower down. A gradual reduction occurs on tracing the sections caudally until the tail region is reached, where a slight increase again takes place.

In *amphibians*, the substantia gelatinosa is poorly developed. The bodies of the horns of mammals are still not completely separated from each other. At the apex of the posterior horn an accumulation of finely myelinated fibres occurs, which may be interpreted as the rudiment of Lissauer's zone. These fibres form a less definite tract in amphibians than in higher animals. There is no great variation in development in the different species examined; nor even in different segments of the cord in the same species. A slight relative increase occurs in the tail region of the cord, with a diminution in the thoracic region, but these are evident only on close examination. No attempt was made to represent them in numerical values.

The posterior funiculi are small, and posterior funicular nuclei have not been definitely recognized.

In *reptiles*, a marked progress towards the condition in mammals occurs. The gray matter has a H-shaped arrangement. The body of the posterior horn is separated from that of the opposite side, and its extremity is surrounded by a well-developed mass of substantia gelatinosa. Lissauer's zone has attained a considerable size, and is easily recognizable, especially at the periphery where the fibres are more closely packed. Between Lissauer's zone and the substantia gelatinosa, and also in the superficial part of the latter, in the upper cervical region of the cord, are bundles of coarsely-myelinated nerve-fibres. Lower down the cord, these coarsely-myelinated fibres diminish very much in number, or completely disappear. Even in man small bundles of coarse fibres are present in the deeper part of Lissauer's zone, or at its junction with the substantia gelatinosa.

In the upper cervical region Lissauer's zone consists of two parts, a superficial, in which the fibres are more closely packed, and a deep, in which the gray matter predominates, but in which scattered, finely-myelinated fibres are present. The gray matter of this part is continuous through the bundles of coarse fibres with that of the superficial part of the substantia gelatinosa. The zone tends to occupy a lateral position. This is well marked in the sacral region of the cord of Dammonia subtrijuga, where it lies midway between the anterior and posterior horns. This may be correlated with the fact, that, in several reptiles, the posterior roots enter, in part, on the lateral side of the posterior horn.

The order of development of the substantia gelatinosa in the reptiles is very irregular. Of the species examined, the crocodile shows the best development, while snakes and turtles show the least. But the orders do not show a strict line of demarcation. Python reticulatus shows a better development of it than Dammonia subtrijuga, while in the Boa constrictor the development is less than in turtles.

As in fishes and amphibians, a decrease in the thoracic region, with a slight relative increase in the caudal region of the cord was noticed in Dammonia. Where the cord enlarges in the cervical and lumbo-sacral swellings, an increase in the substance also occurs.

The posterior funiculi are well developed, and posterior funicular nuclei are recognizable.

In *birds*, the development is well marked in the upper part of the cord. Caudal to the lumbo-sacral sinus, the cord becomes very small, and the posterior horns very slender, and relatively very much decreased in size, and the substantia gelatinosa is here not well developed. In other respects they conform to the description given for reptiles. The posterior funiculi are, however, relatively much smaller.

In *mammals*, substantia gelatinosa was recognizable in all the species examined. In Xantharpya amplexicaudata and Macropus robustus it is very well developed; in Tursio tursiops and Phocaena communis it is poorly developed. It surrounds the body of the posterior horn like a cortex (KAPPERS, 1914) or cap. It reaches its maximum size in the lower end of the cord, where in the sacral region and in the conus (SANO, 1909) it occupies, in many species, the entire posterior horn. While an increase in amount occurs in the cervical swelling, the relative development at this point may be less than in the cord higher up.

Lissauer's zone stretches from the substantia gelatinosa to the surface of the cord (the bottom of the postero-lateral sulcus), and may also show extensions into the lateral funiculus (LESZLÉNYI, 1912 ; SANO, 1914). This lateral extension is not marked in the case of Hylobates, but is evident in Simia satyrus, as a triangular area, with its base at the posterior horn and its apex extending into the lateral funiculus. Both the substantia gelatinosa and Lissauer's zone are irregularly developed throughout the mammals.

We see from the above description that substantia gelatinosa is an important constituent of the afferent side of the cord in lower vertebrates. It is recognizable as soon as a posterior horn is differentiated, and it forms the entire constituent of the horn. Assuming that the corpus commune posterius of fishes is homologous to the fused bodies of the posterior horns of higher vertebrates, we see that in the lower forms the substantia gelatinosa is relatively more important than in the higher forms, though it is still well developed in the latter, especially in the sacral region of the cord, where it fills, in man and some other forms, the entire posterior horn.

Lissauer's zone appears to be closely related phylogenetically to the substantia gelatinosa. It originates in the superficial gray matter of the posterior horn in amphibians, and contains nerve cells in all species. Its development, however, does not always run parallel to that of the substantia gelatinosa (see page 4).

Conclusions.

In how far does this description fit in with the present views on the functions of these parts of the cord? SANO (1909) made an extensive comparative study of the substantia gelatinosa in mammals, but found no well defined lines of development which might give a clue to its function. He compiled tables showing the relative development of the substantia gelatinosa to that of the total area of cross section, the white, and gray matter at the principal levels in the cords of twenty five species of mammals, but on comparison of his figures he found the resulting order offered little in the way of explanation of its function. He suggested a possible sympathetic function. In animals with long large intestines, he considered that the substance should show an enlargement corresponding to the increased sympathetic innervation. This was not the case.

In view of the demonstration by TAKAHASHI (1913) of gelatinous substance in the lateral horn of the cord, which is generally believed to have a sympathetic function, and the continuity of the substance with the Rolandic substance of the posterior horn, together with the presence of sensory sympathetic fibres in the posterior roots, this suggestion of SANO is interesting. There is no evidence, however, that fishes, such as Albula vulpes and Mormyrus cashive, where the substantia gelatinosa far surpasses in relative size that of mammals, have a corresponding development of the sympathetic system. In fact, such is very unlikely. In the thoracic region of the cord of mammals where sympathetic fibres are very numerous, the substantia gelatinosa is, on the other hand, least developed.

RANSON's theory (1914, 1915, etc.) on its function seems to me to offer the best explanation in the light of our present knowledge, and it receives most support on phylogenetic study. He divides sensation, following HEAD and SHERREN (1905), into protopathic and epicritic. Protopathic sensation, he believes, is associated with the substantia gelatinosa, while epicritic chiefly passes upwards in the cord, by way of the posterior funiculi.

In lower animals where protopathic sensation is practically the only kind present we should expect to find the posterior funiculi small or absent, and the substantia gelatinosa developed in proportion to the actual sensitivity of the animal. In fishes, the posterior funiculi form about 5 % of the total white substance of the cord, whereas in mammals, they form from 14.5 % in Sorex vulgaris to 38.91 % in man (BROUWER, 1915). Further, in Albula, where, as already stated, the gelatinous substance is very well developed, there is evidence of a great cutaneous sensation in the presence of a large cutaneous branch of the facial nerve (VAN DER HORST, 1928), and in the habits of the animal. It lives in shallow water and seeks its food in the sands and gravel. Malapterurus electricus, on the other hand, in which the substance is very poorly developed, is covered with a thick coat of gelatinous-like material, is of slow motion, and strongly electrical. On account of the presence of both forms of sensation in higher animals the picture must necessarily be obscure, and this may account for the irregularity of SANO's findings.

In favour of the substantia gelatinosa being related not merely to the protopathic sensation of the viscera, but also to the protopathic sensation of the skin is the fact, that this substance is so poorly developed in the dolphin, where it cannot be assumed that visceral sensation is less, but where a smaller skin sensation is very likely on account of the reduction in the hind roots and cutaneous nerves in general.

RANSON (1911) demonstrated, in the peripheral nerves, the presence of unmyelinated fibres, which outnumber the myelinated fibres, later (1913) he showed that the unmyelinated fibres group themselves in the lateral part of the posterior root at the point where the latter enters the cord. These unmyelinated fibres, together with some finely-myelinated, enter Lissauer's zone, and after a short course in this zone end in the substantia gelatinosa. WINDLE (1923) demonstrated the occurrence of unmyelinated fibres in the posterior roots between the cord and the spinal ganglia, and (1926) showed that in the trigeminal nerve unmyelinated fibres pass downwards, without bifurcating, in the descending root. He also showed, in the same year, the presence of these fibres in the peripheral branches of the trigeminal nerve. RANSON (1915) and RANSON and BILLINGSLEY (1916) interpret these unmyelinated fibres as the conductors of protopathic sensation.

In conclusion, I wish to thank Professor KAPPERS for having directed my attention to this subject, and for his many kindnesses and advice while the work was in progress. I also wish to thank Dr. ADDENS for his invaluable assistance, and the Staff of the Central Institute generally for the readiness with which they help the research worker, and place the great resources of the Institute at his disposal.

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Anatomy. — *The pars magnocellularis of the nucleus preopticus in Amphibia, particularly in Urodela*. By H. H. CHARLTON. University of Missouri School of Medicine and Central Dutch Institute for Brain Research, Amsterdam, Holland. (Communicated by Prof. C. U. ARIËNS KAPPERS.)

(Communicated at the meeting of April 27, 1929).

Although HERRICK ('10) described in Amblystoma tigrinum a vertical sulcus dividing the preoptic nucleus into rostal and caudal portions which he termed the pars anterior and the pars magnocellularis of the preoptic nucleus, the fact seems to have been lost sight of, particularly in view of the extensive work done on this nucleus by RÖTHIG ('11), who failed to observe a pars magnocellularis in his Urodele material. The only figure showing the large-celled part of the preoptic nucleus is one by HERRICK ('17) showing its position in Necturus maculatus as seen in a cross section through its caudal portion.

In a recently prepared series of Cryptobranchus alleghaniensis and of Amphiuma means, cut transversely 20 micra in thickness and arranged in an alternate series, one stained in DELAFELD's haematoxylin and the other by the method of WEIGERT, the pars magnocellularis is exceedingly well defined. In addition to these two series prepared by the writer, there was at the Central Dutch Institute for Brain Research a beautiful Cajal silver series of the Giant Salamander of Japan and China, Cryptobranchus japonicus, as well as other good slides of Urodela and Anura.

Fig. 1 is a low power drawing through the brain of Cryptobranchus alleghaniensis in the region where the pars magnocellularis is most prominent. Here the nucleus extends from the level of the sulcus diencephalicus ventralis nearly to the floor of the preoptic recess. In order to bring out the details of the cells, the area shown in the small rectangle in fig. 1 is reproduced in fig. 2 under higher magnification. The large cells are spheroidal or oval in shape and measure in their longest diameter about 24 micra, contrasting with the small cells, which measure 12 micra.

The cells stand out not only because of the difference in nuclear size, but to a certain extent because of their faintly stained appearance in contrast to the more pycnotic appearance of the cells of the pars parvocellularis. The nucleus magnocellularis as a whole begins high up on the wall of the preoptic recess and descends to the bottom almost immediately. Its upper limits follow the sulcus diencephalicus ventralis and its depth becomes less with each succeeding section until it terminates near the level of the caudal part of the habenular commissure. At first the pars magnocellularis is located between the ependymal cells of the preoptic recess and the pars parvo-cellularis. Later, as the nucleus leaves the floor of the recess most of

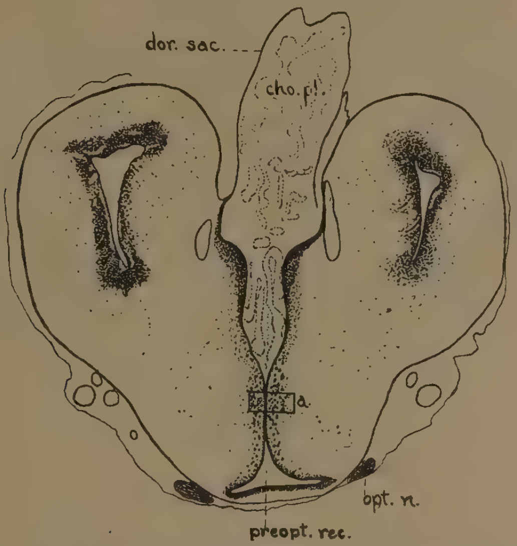

Fig. 1. Cryptobranchus alleghaniensis. Cross section through the diencephalon near the entrance of the optic nerves. × 18. *a*, Rectangular area through the preoptic nucleus shown under higher magnification in figure 2; *opt. n.*, optic nerve; *preopt. rec.*, preoptic recess; *cho. pl.*, choroid plexus; *dor. sac.*, dorsal sac.

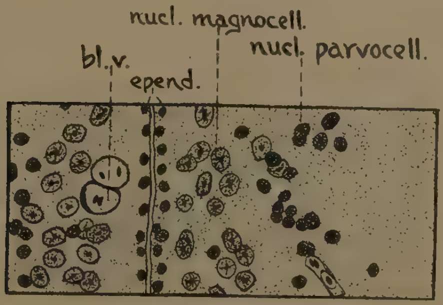

Fig. 2. Cryptobranchus alleghaniensis. Area shown in rectangle (a) of figure 1. × 180. *nucl. magnocell.*, nucleus preopticus pars magnocellularis; *nucl. parvocell.*, nucleus preopticus pars parvocellularis; *bl. v.*, blood vessels; *epend.*, ependyma lining the preoptic recess.

the cells seem to be of the large cell type, with but a slight intermingling of the smaller cells. In my slides most of the cell nuclei seem to be bare of cytoplasm, but in a few cells a small quantity seems to partially surround the nucleus.

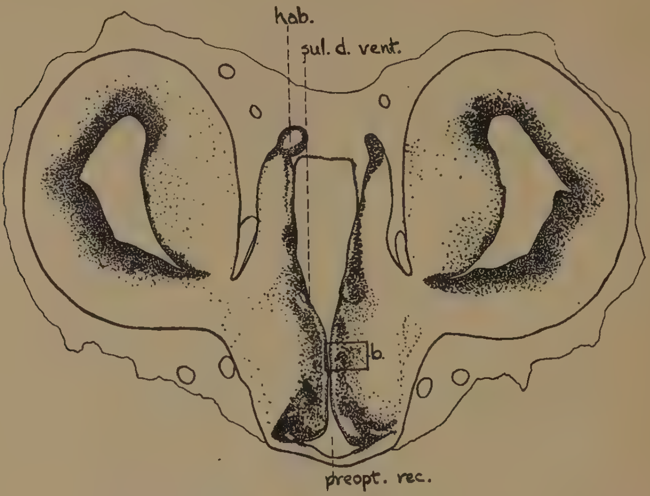

Fig. 3. Amphiuma means. Cross section through the preoptic recess at the level shown by line *A—B* in figure 7. × 17. *b.*, Rectangular area through the preoptic nucleus shown under higher magnification in figure 4; *preopt. rec.*, preoptic recess; *hab.*, habenula; *sul. d. vent.*, sulcus diencephalicus ventralis.

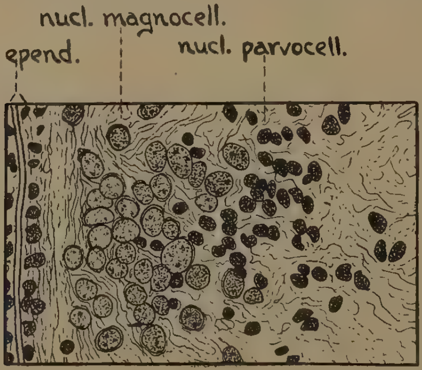

Fig. 4. Amphiuma means. Area shown in rectangle (*b*) of figure 3. × 180. *nucl. magnocell.*, nucleus preopticus pars magnocellularis; *nucl. parvocell.*, nucleus preopticus pars parvocellularis; *epend.*, ependyma lining preoptic recess.

A similar series of drawings has been made of the brain of Amphiuma means, (figs. 3 and 4). Here the contrast in cell size is considerably greater than in Cryptobranchus alleghaniensis. The diameter of the pars magnocellularis cells is from 20 to 30 micra, the size increasing as one follows the nucleus caudally. The pars parvo-cellularis cells measure 15 micra in their greatest diameter. The large cells are for the most part spherical, showing a narrow ring of cytoplasm around the nucleus. Although the nucleus at its most prominent region extends practically to the floor of the preoptic recess, it does not extend along the lateral branch of the preoptic recess at all.

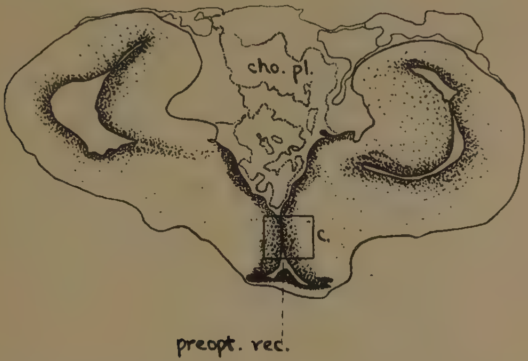

Fig. 5. Cryptobranchus japonicus. × 18. Cross section through the diencephalon at about the same level as shown in figure 1. c. Rectangular area through the preoptic nucleus shown under higher magnification in figure 6. *Cho. pl.*, choroid plexus; *preopt. rec.*, preoptic recess.

In Cryptobranchus japonicus the nucleus magnocellularis is shown under high magnification in fig. 6, (for level and position of drawing see fig. 5). The large cells are first seen anteriorly near the middle level, dorso-ventrally of the recess wall. Traced caudally they soon reach the floor and run along the lateral pockets of the preoptic recess. This ventro-lateral extension of the nucleus, greater here than in either Cryptobranchus alleghaniensis or Amphiuma means, is the usual arrangement in fishes, where the nucleus usually begins in front in this ventro-lateral position.

Tracing the nucleus caudally, it has the same characteristics as seen previously in Cryptobranchus alleghaniensis and Amphiuma means except that it ends almost as soon as it reaches the caudo-dorsal position instead of extending caudally for some distance as a thin strand of cells.

The nucleus, however, differs quite markedly from that of the other Urodela described, in at least two particulars. First, the cells are few and scattered among the numerous pars parvo-cellularis cells of the nucleus preopticus. In the region figured, the cell number is about one half that of Cryptobranchus alleghaniensis and only one fourth that of Amphiuma means. The variations in cell size are not great, since we find here a diameter roughly of 26 micra, compared to 24 in Cryptobranchus alleghaniensis and 30 in Amphiuma, measuring the longest observed cells in each case. Much more striking, however, is the second difference, i. e., nuclear size. Here the nucleus has a diameter of 15 micra, or only about one half the size of the cell, while in Cryptobranchus alleghaniensis it is 24 and in Amphiuma means 28. In the last two forms the cytoplasm is reduced to a mere vestige. We have, therefore, here in Cryptobranchus japonicus a small nucleus surrounded by a relatively large amount of cytoplasm standing in sharp contrast to the large nucleus in Amphiuma means which on the contrary has but little cytoplasm. The nuclei of the large cells of Crytobranchus japonicus do not differ greatly in size from those of the pars parvocellularis. This may explain why RÖTHIG ('11) did not report the presence of the nucleus in this form, for unless one were particularly fortunate in getting a good cytoplasmic fixation, the nucleus magnocellularis would be lost among the cells of the pars parvocellularis.

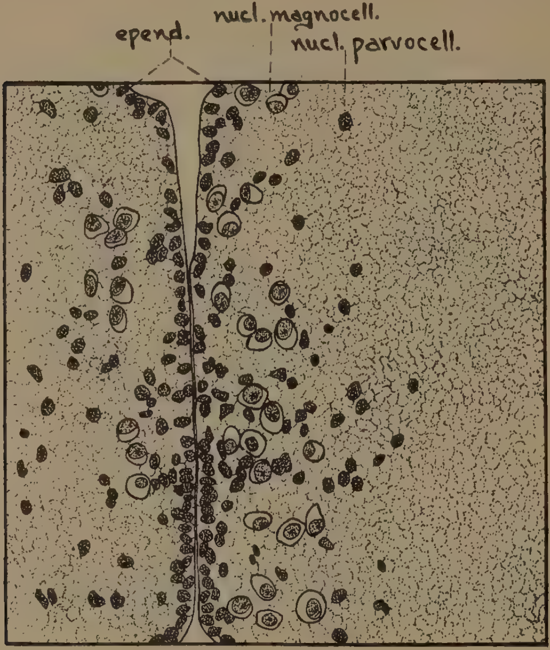

Fig. 6. Cryptobranchus japonicus. Area shown in rectangle *c* of figure 5. × 150. *Epend.* ependyma; *nucl. magnocell.*, nucleus preopticus pars magnocellularis; *nucl parvocell.*, nucleus preopticus pars parvocellularis.

HERRICK ('10, fig. 22) has indicated the position in Amblystoma tigrinum of a number of sulci seen on the lateral wall of the thalamic and hypothalamic regions. According to this writer the sulcus limitans ends somewhere in the floor of the preoptic recess. In order to compare the

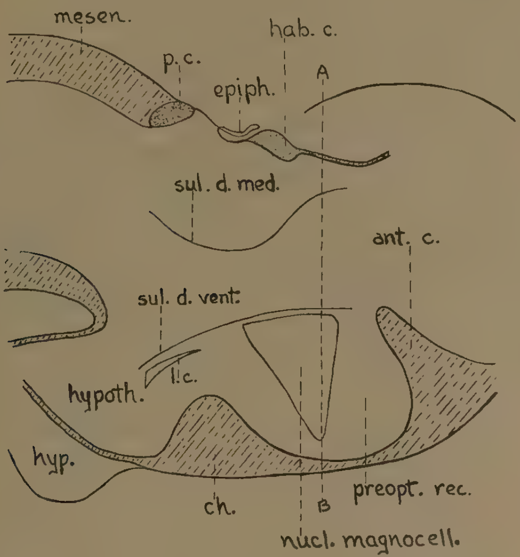

Fig. 7. Amphiuma means. A schematic sagittal section. × 17. *p. c.*, posterior commissure; *hab. c.*, habenular commissure; *epiph.*, epiphysis; *mesen.*, mesencephalon; *sul. d. vent.*, sulcus diencephalicus ventralis; *sul. d. med.*, sulcus diencephalicus medialis; *ant. c.*, anterior commissure; *preopt. rec.*, preoptic recess; *nucl. magnocell.*, nucleus preopticus pars magnocellularis; *l.c.*, large cells; *ch.*, optic chiasma; *hyp.*, hypophysis; line *A—B* represents plane of section of figure 3. *hypoth.*, hypothalamus.

preoptic region in Amphiuma means with HERRICK's Amblystoma figure, a schematised sagittal section is shown in fig. 7. This may also be compared to OSBORN's ('83) figure *H* of a sagittal section through the brain of Amphiuma. The sulcus limitans does not appear with any degree of certainty in any of the forms described above, but it is of some interest to note that the postero-ventral limits of the nucleus in Amphiuma means seem to coincide almost exactly with the ventral limb of the sulcus limitans as figured by HERRICK. This being true, we can describe the nucleus as holding an antero-dorsal position with reference to the sulcus limitans, and if we can still speak at this level of alar and basal plates, then the pars magnocellularis is located in the dorsal, or alar, division.

The cells of the pars magnocellularis are in Amphiuma means of so striking a character that the appearance of similar cells located just below the sulcus diencephalicus ventralis as one traces it into the hypothalamus is clearly recognizable. These cells are relatively few in number and reach their maximum near the level of the beginning point of the recessus lateralis hypothalami. Their position is indicated in fig. 7. HOLMGREN ('20) has called attention to large cells holding the same position in Teleostei. These he finds to be similar in type to the cells of the nucleus magnocellularis and suggests that they may have a similar function.

The nucleus magnocellularis is of such prominence in fish that rarely indeed does one have trouble in recognizing it. In the Urodele group of Amphibia this does not seem to be so easy, for RÖTHIG ('11) did not observe it in Spelerpes fuscus, Cryptobranchus japonicus, Necturus maculatus, Siren lacertina, Diemyctylus viridescens, and Hynobius. In his paper on the phylogenesis of the hypothalamus RÖTHIG ('11) writes as follows: "Der Nucleus praeopticus ist die Zellansammlung, die den Recessus praeopticus umgiebt. Sie besteht bei den Urodelen aus gleichartigen, kleinen, runden Zellen, während die Anuren eine kleinzellige und eine grosszellige Abteilung besitzen; die erstere liegt mehr frontal, die letztere mehr caudal". His figures for the size of the large cells in Rana are given as 15 micra, and for the small cells 6 to 8 micra. In Amphiuma means, as previously noted, the magnocellular cells may reach fully 30 micra in diameter and the parvocellular cells about 12 micra.

Yet the nucleus magnocellularis is present in Necturus maculatus and in Amblystoma tigrinum, HERRICK ('10 and '17). By the aid of the camera lucida, cell size differences have been noted by the writer in Necturus maculatus (corroborating the findings of HERRICK), in the cave salamander, Typholotriton spelaeus, and in Molge cristata, but the differences in the first two were not sharp enough to make a complete nuclear study and in Molge cristata only a few large cells were observed. These differed however quite markedly from the parvocellular cells both in size and appearance. The writer ('24) considered the Urodela exceptional in that they did not possess a pars magnocellularis division of the preoptic nucleus. This view is no longer tenable. That the nucleus may be lacking in some Urodele forms is doubtful in view of the present findings, but that it may be difficult of detection is quite apparent from the previously mentioned work of RÖTHIG and from my own experience. In the present study it has been impossible to make out cell size variations or cells giving a distinctly different stain reaction, in Bombinator pachypus, Proteus anguinus, Salamandra maculosa, and Axolotl.

If it should be found that the nucleus magnocellularis appears only late in brain development, it might explain some failures recorded. Either that, or the necessity for a more rapid fixative than the usual formalin mixtures, may be indicated.

In order to compare the position and length of the nucleus as found in the Urodela with that of fish, where it is a constant finding, and with the Anura, the nuclei of several representatives of each group have been charted in relation to the anterior commissure and the place of exit of the third or oculomotor nerve. The method of KAPPERS ('20 and '21) for comparing the position and shifting of the cranial nerve nuclei has been slightly modified for use here. The results are given in fig. 8.

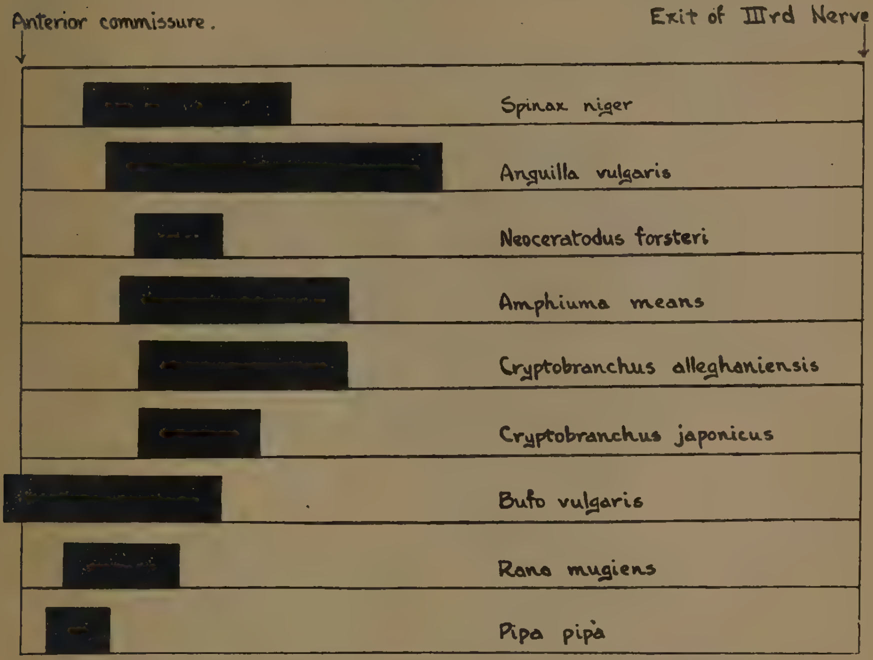

Fig. 8. This chart indicates the position and length of the nucleus preopticus pars magnocellularis in Selachians, Teleostei, Dipnoi, Urodela and Anura in relation to the anterior commissure and the place of exit of the fibres of the third nerve.

In the three Urodele forms charted, Amphiuma means, Cryptobranchus alleghaniensis, and Cryptobranchus japonicus, the nucleus has about the same relation to the anterior commissure but decreases in length in the above order, being in the latter only slightly more than one half as long as in the other two.

The nucleus has been charted in three fishes, Spinax niger, a Selachian, Anguilla vulgaris, a Teleost, and Neoceratodus forsteri, a Dipnoan. The first differs but little from our findings in the Urodela. Anguilla vulgaris has a longer nucleus magnocellularis than the average Teleost, and its cells are among the largest found in that group, measuring from 40—60 micra. The nucleus of these giant cells has a diameter of from 10—15 micra. But when compared to the Urodela the chief difference is a longer drawn out strand of cells extending caudo-dorsally from the nucleus proper. An examination of fig. 9 shows the prominent nucleus of closely packed large cells lining the preoptic recess throughout its entire extent. The nucleus is quite short in Neoceratodus forsteri, in fact quite the shortest except for that in Pipa pipa.

When we compare the position and length of the nucleus magnocellularis

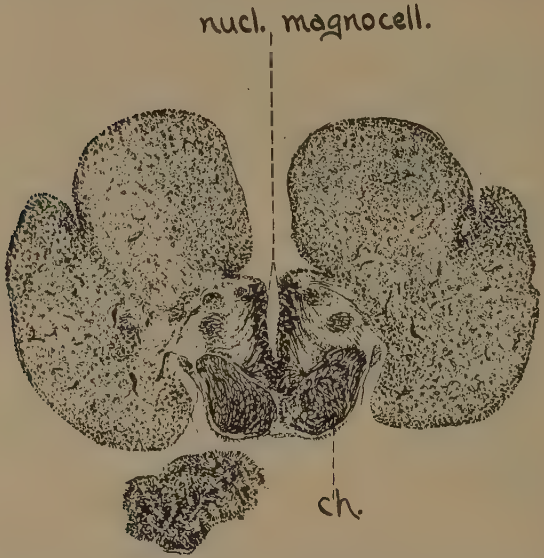

Fig. 9. Anguilla vulgaris. Cross section through the preoptic recess. × 60. *nucl. magnocell.*, nucleus preopticus pars magnocellularis; *ch.*, optic chiasma.

(fig. 8) in Urodela with that in Anura it will be seen at once to have a more caudal beginning in the Urodela. As for length, that in Bufo vulgaris is somewhat longer, but in both Rana catesbyana (mugiens) and Pipa pipa it is shorter. As the brain structure is much compressed in Pipa pipa and in the Anura in general, this compression, reduced in my charts should give rise to a larger extent of its field, thus making the nucleus appear relatively longer. Since this is not the case, its shortness in these two forms of Anura is but accentuated. In Bufo vulgaris the nucleus, while long, is narrow dorso-ventrally, never lining the entire extent of the preoptic recess at any one level. Furthermore, the nucleus in Bufo vulgaris and Rana catesbyana near its caudal termination bends or turns laterally to end quite some distance from the preoptic recess. OSBORN ('83) calls attention to the gross similarity of the infundibulum in Amphiuma to that found in Teleostei. It certainly seems true also that the nucleus magnocellularis in the Urodela is more similar to that of Teleostei than to the Anura as judged by length, height or dorso-ventral extent, and the position of the beginning point.

Of what significance is the anterior position of the nucleus in Anura? Is it correlated in any way with a terrestial life? The fact that it is located still more anteriorly in birds would seem to confirm this last view point. Or is it perhaps a consequence of the telescoping of the forebrain and the anterior commissure over the betweenbrain as also occurs in birds? (cf. KAPPERS '20, Vol. II). But why should such closely related forms as Cryptobranchus alleghaniensis and Cryptobranchus japonicus show such nuclear length variations? The nucleus magnocellularis is not only short in Cryptobranchus japonicus, but the cells are much fewer in number and are rather scattered.

GADOW ('01) states that Cryptobranchus japonicus differs from Cryptobranchus alleghaniensis in one essential point only, namely, by the absence of gill openings and of the modifications of the branchial apparatus connected therewith. Cryptobranchus japonicus lives in mountain streams and has been found 4500 feet above sea level. The respiration rate under aquarium conditions is, according to TEMMINCK and SCHLEGEL [1]) once every 6—10 minutes. It would be interesting to know the respiratory rate in Cryptobranchus alleghaniensis.

CONCLUSIONS.

I. A distinct and prominent pars magnocellularis of the nucleus preopticus occurs in the Urodele forms Cryptobranchus alleghaniensis, Cryptobranchus japonicus, and Amphiuma means. It has been observed in a lesser degree in Necturus maculatus, Typhlotriton spelaeus, and in Molge cristata, and is probably present in other Urodela.

II. The cells and nuclei of the cells are the largest in Amphiuma means. Cryptobranchus japonicus, on the other hand, has cells with small nuclei but a much greater amount of cytoplasm.

III. The nucleus is limited dorsally by the sulcus diencephalicus ventralis and its caudo-ventral limits follow a curve quite like that shown by many authors for the rostal termination of the sulcus limitans.

IV. The nucleus in Urodela resembles its counterpart in the fishes in its position, length, and cell size, more than it does that in its nearer relatives, the Anura, which is correlated perhaps with a life spent almost wholly in the water.

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Mathematics. — *Anzahlbestimmung der rationalen Kurven fünfter Ordnung, die durch zehn gegebene Punkte des Raumes gehen.* By G. SCHAAKE. (Communicated by Prof. JAN DE VRIES.)

(Communicated at the meeting of March 23, 1929.)

1. Dr. J. W. VAN KOL hat mir die folgende Methode angegeben zur Anzahlbestimmung der rationalen Kurven vierter Ordnung k^4, die durch acht gegebene Punkte $P_1, \ldots, P_8$ des Raumes gehen.

Wir denken uns zwei Geraden l_1 und l_2, die mit $P_1, \ldots, P_7$ auf einer quadratischen Fläche φ^2 gelegen sind, derart dass l_1 und l_2 zu derselben Regelschar von φ^2 gehören und wir bestimmen die Anzahl der rationalen Kurven k^4, die durch $P_1, \ldots, P_7$ gehen und l_1 und l_2 schneiden.

Die durch $P_1, \ldots, P_7$ bestimmte Kurve (3,1) von φ^2, die jede Gerade l der l_1 und l_2 enthaltenden Regelschar von φ^2 dreimal und jede Gerade der anderen Regelschar von φ^2 einmal schneidet, soll neunmal, die durch $P_1, \ldots, P_7$ bestimmte Kurve (1,3) von φ^2 einmal und jede der 12 rationalen Kurven (2,2) durch $P_1, \ldots, P_7$ viermal gerechnet werden. Die gesuchte Anzahl ist also 58.

Ist m_1 eine Gerade der Regelschar (m), so finden wir, dass es 54 rationale Kurven k^4 giebt, die durch $P_1, \ldots, P_7$ gehen und l_1 und m_1 in verschiedenen Punkten schneiden. Es giebt also vier rationale Kurven k^4, die durch $P_1, \ldots, P_7$ und $l_1\, m_1$ gehen.

2. Wir wollen mit Hilfe der in § 1 angegebenen Methode die Anzahl bestimmen der rationalen Kurven fünfter Ordnung, die durch zehn gegebene Punkte $P_1, \ldots, P_{10}$ des Raumes gehen.

Nun denken wir uns zwei Geraden l_1 und l_2, die mit $P_1, \ldots, P_9$ auf der quadratischen Flache φ^2 gelegen sind, derart dass l_1 und l_2 zu derselben Regelschar von φ^2 gehören und wir bestimmen die Anzahl der rationalen Kurven k^5, die durch $P_1, \ldots, P_9$ gehen und l_1 und l_2 schneiden. Die durch $P_1, \ldots, P_9$ bestimmte Kurve (4,1) von φ^2 soll sechzehnmal, die durch $P_1, \ldots, P_9$ bestimmte Kurve (1,4) von φ^2 soll einmal gerechnet werden.

Die Punkte $P_1, \ldots, P_9$ bestimmen ein Netz von Kurven (3,2). Dieses Netz enthält eine endliche Anzahl von rationalen Kurven, das sind die irreduziblen Kurven dieses Netzes, die zwei Doppelpunkte besitzen. Diese sollen neunmal gezählt werden.

Wenn wir diese Kurven (3,2) aus P_1 auf eine Ebene α projizieren, bekommen wir das Netz der biquadratischen Kurven k'^4, die alle einen Doppelpunkt haben im Spurpunkte der P_1 enthaltenden Gerade l von φ^2

und die durch die Projektionen $P'_2, \ldots, P'_9$ von $P_2, \ldots, P_9$ und durch den Spurpunkt der P_1 enthaltenden Gerade m von φ^2 gehen. Wir haben die Anzahl der rationalen Kurven k'^4 dieses Netzes zu bestimmen, das ist die Anzahl der irreduziblen Kurven dieses Netzes, die noch zwei Doppelpunkte besitzen.

Zur Bestimmung dieser Anzahl benutzen wir die Abbildung einer biquadratischen Fläche F^4_2 mit einer Doppelgerade d auf eine Ebene φ, deren Eigenschaften in R. STURM: *Die Lehre von den geometrischen Verwantschaften* IV [926] beschrieben sind. Die ebenen Durchschnitte von F^4_2 werden nämlich abgebildet auf die ∞^3 Kurven c'^4 von φ, die einen gegebenen Doppelpunkt und acht feste einfache Punkte besitzen. Das Netz der Kurven c'^4, die noch einen neunten gegebenen einfachen Punkt haben, ist also das Bild des Systems der ebenen Durchschnitte von F^4_2, die durch einen gegebenen Punkt A dieser Fläche gehen und die Kurven c'^4 des genannten Netzes, die noch zwei Doppelpunkte besitzen, sind die Abbildungen der ebenen Durchschitte von F^4_2 mit den durch A gehenden doppelten Berührungsebenen.

Wenn wir aus A projizieren, so ist der wahre Umriss eine Kurve zehnter Ordnung k^{10}, die in A einen Doppelpunkt hat und d sechsmal schneidet, nämlich in den vier Kuspidalpunkten und in den beiden Berührungspunkten der Ebene Ad. Ihre Projektion auf eine Ebene β, der scheinbare Umriss von F^4_2, ist eine Kurve achter Ordnung k'^8, die von der zwanzigsten Klasse ist, wie die Fläche F^4_2. Die Kurve k'^8 besitzt Rückkehrpunkte in den Spurpunkten der durch A gehenden Haupttangenten, die F^4_2 in von A verschiedenen Punkten berühren.

Die zweite Polarfläche von A schneidet k^{10} in 20 Punkten; zwei dieser Punkte sind die Berührungspunkte der Ebene Ad und sechs fallen in A. Die Kurve k'^8 hat also zwölf Rückkehrpunkte. Hieraus folgt, dass k'^8 keine Doppelpunkte hat, was auch unmittelbar deutlich ist.

Die Anzahl der Wendetangenten von k'^8 ist: $3 \times 8 \times 6 - 8 \times 12 = 48$ und die Anzahl der Doppeltangenten ist folglich $^1/_2\,(20 \times 19 - 8 - 144) = 114$.

Durch A gehen also 114 doppelte Berührungsebenen von F^4_2. Hierzu gehören die Ebene Ad und die Ebenen durch A und die sechzehn von d verschiedenen Geraden von F^4_2. Diese siebzehn Ebenen sollen ausgesondert werden, weil die deren Durchschnitten mit F^4_2 korrespondierenden Kurven c'^4 zusammengesetzt sind aus einer Gerade und einer kubischen Kurve vom Geschlechte eins.

Wir finden, dass es 96 rationale biquadratische Kurven giebt, die einen festen Doppelpunkt und neun mit diesem Punkte in einer Ebene gelegene feste einfache Punkte besitzen. Folglich enthält eine Fläche zweiter Ordnung 96 rationale Kurven (3,2), die durch neun Punkte dieser Fläche gehen.

Die 96 durch $P_1, \ldots, P_9$ bestimmten rationalen Kurven (3,2) von φ^2 sollen zur Bestimmung der gesuchten Anzahl neunmal gerechnet werden und jede der 96 durch $P_1, \ldots, P_9$ bestimmten Kurven (2,3) von φ^2 soll viermal gerechnet werden. Wir flnden also $16 + 1 + 13 \times 96 = 1265$ rationale Kurven k^5, die durch $P_1, \ldots, P_9$ gehen und l_1 und l_2 schneiden.

Wenn wir statt l_2 eine Gerade m_1 der zweiten Regelschar von φ^2 nehmen, so finden wir, dass es $4 + 4 + 12 \times 96 = 1160$ Kurven k^5 giebt, die durch $P_1, \ldots, P_9$ gehen und l_1 und m_1 in verschiedenen Punkten schneiden.

Hieraus folgt, dat es 105 rationale Kurven k^5 giebt, die durch $P_1, \ldots, P_8$ und $l_1\, m_1$ gehen.

Es giebt also 105 rationale Kurven k^5, die durch zehn allgemein gelegene Punkte des Raumes gehen.

Mathematics. — *Ueber involutorische Punkttransformationen im konformen Raum.* Von H. BECK in Bonn. (Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of March 23, 1929).

1. In einer Note: On an involution among the rays of space [1]) hat Herr JAN DE VRIES eine involutorische Geradentransformation beschrieben. die nicht nur an sich interessant ist, sondern den Weg zu einer grossen Anzahl weiterer solcher involutorischen *Geraden*transformationen des dreidimensionalen *projectiven* Raumes eröffnet, wie im Folgenden gezeigt werden soll. Ausserdem lässt sich aus dem Ansatz von Herrn J. DE VRIES noch eine ganze Anzahl von involutorischen *Punkt*transformationen des dreidimensionalen *konformen* Raumes gewinnen.

2. Herr J. DE VRIES geht von vier Geradenbüscheln aus, Eine Gerade G des Raumes trifft eine Gerade jedes der vier Büschel und die andere Quadrisekante dieser vier letztgenannten geraden Linien ist die zu G zugeordnete Gerade G'.

Bildet man jetzt in bekannter Weise die geraden Linien des Raumes auf die Punkte einer singularitätenfreien $M_4{}^2$ eines R_5 ab, so hat man auf dieser $M_4{}^2$ vier gerade Linien (den Büscheln entsprechend) und einen Punkt (der Geraden G zugeordnet). Der Tangential-R_4 in diesem Punkte schneidet jede der vier geraden Linien in einem Punkte. Durch die so gewonnenen vier Punkte läuft dann noch ein anderer Tangential-R_4 von $M_4{}^2$, und sein Berührungspunkt entspricht der Geraden G'.

3. Jetzt ersetzen wir die $M_4{}^2$ durch eine singularitätenfreie $M_3{}^2$ eines R_4. Auf dieser nehmen wir *drei* gerade Linien G_1, G_2, G_3 an, und einen Punkt p. Der Tangential-R_3 in p wird von G_1, G_2, G_3 in den Punkten p_1, p_2, p_3 geschnitten. Durch die Punkte p_1, p_2, p_3 *läuft noch ein weiterer* Tangential-R_3 vom Berührungspunkt p'. Dann ist die Beziehung zwischen den Punkten p und p' involutorisch.

4. Der *konforme* dreidimensionale Raum hat den Zusammenhang einer singularitätenfreien $M_3{}^2$. Man stellt den "eigentlichen" Punkt mit den rechtwinkligen kartesischen Koordinaten (ξ, η, ζ) durch fünf Koordinaten $x_0 : x_1 : x_2 : x_3 : x_4$ dar:

$$\xi = \frac{x_1}{x_0 + x_4}, \quad \eta = \frac{x_2}{x_0 + x_4}, \quad \zeta = \frac{x_3}{x_0 + x_4}.$$

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[1]) Diese Proceedings, Vol. 22, p. 478.

Zwischen den konformen Koordinaten des Punktes besteht dann die Relation

$$x_0^2 - x_1^2 - x_2^2 - x_3^2 - x_4^2 = 0,$$

und diese liefert die $M_3{}^2$, wenn die x als homogene Punktkoordinaten in einem R_4 gedeutet werden. Die Punkte x von $M_3{}^2$, für die $x_0 + x_4 = 0$ ist, liefern die nicht eigentlichen oder *akzessorischen* Punkte des konformen Raumes, die sich nicht durch (ξ, η, ζ)-Koordinaten darstellen lassen.

Den geraden Linien auf $M_3{}^2$ entsprechen dann die *Isotropen* des konformen Raumes, wobei unter einer Isotrope verstanden werden soll eine *Minimalgerade oder eine Tangente* (aber nicht Bisekante) *des imanären Kugelkreises.* Zwei Punkte auf einer Isotropen sollen *zueinander parallel* genannt werden.

5. Danach lässt sich die Konstruktion von § 3 folgendermassen in den konformen Raum übertragen: *Gegeben ist ein Punkt p und drei Isotrope G_1, G_2, G_3. Auf jeder von ihnen liegt ein zu p paralleler Punkt. Diese drei Punkte bestimmen einen Kreis, der p zum Scheitel* (CHASLES) *hat* [1]. *Der andere Scheitel p′ dieses Kreises ist dem Punkte p involutorisch zugeordnet.*

6. Um jetzt die Einzelheiten dieser involutorischen Punkttransformation des konformen Raumes verfolgen zu können, haben wir die Isotropentripel G_1, G_2, G_3 gegenüber konformen Transformationen zu klassifizieren. Das gibt fünf Typen solcher Tripel.

a. Drei Isotrope auf einer speziellen Kugel (d. i. auf einem Minimalkegel, einer Minimalebene, oder endlich drei Tangenten des imaginären Kugelkreises). Hier artet die Transformation aus; der Punkt p' hat, so lange er überhaupt eindeutig bestimmt ist, nicht ∞^3, sondern nur eine einzige Lage (z. B. Doppelpunkt des Minimalkegels).

b, c. Drei Isotrope auf einer nicht speziellen Kugel (d. i. auf einer Kugel im eigentlichen Sinne des Wortes, oder auf einer Euklidischen Ebene).

Hier reduziert sich die Transformation auf die *Inversion* an der Kugel.

d. Zwei sich schneidende Isotrope sind zu einer dritten windschief [2].

e. Drei windschiefe Isotrope, die keiner Kugel angehören. Es gibt jedesmal nur eine einzige Klasse dieser Isotropentripel, d. i. das Isotropentripel besitzt keine absolute konforme Invariante. Den Fall *e* werden wir nicht mehr zu behandeln nötig haben, weil der Fall *d* bereits eine viel weiter reichende Verallgemeinerung liefert.

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[1] Die Scheitel eines Kreises sind also die Punkte, die gleichzeitig zu allen Punkten des Kreises parallel sind.

[2] Parallele Minimalgerade gelten nur dann als sich schneidende Isotrope, wenn sie die Minimalebene gemeinsam haben.

7. Im Falle d lassen sich drei Isotropen immer durch konforme Transformation in folgende Lagen bringen

$$G_1;\quad \lambda:\mu:i\mu:0:-\lambda \qquad G_2;\quad \lambda:\mu:-i\mu:0:-\lambda$$
$$G_3;\quad \lambda:0:\mu:i\mu:\lambda.$$

Wir haben also einen veränderlichen Punkt der Isotropen durch zwei homogene Parameter $\lambda:\mu$ dargestellt. Die Isotropen G_1 und G_2 schneiden sich im Punkte $1:0:0:0:-1$. Dieser ist parallel zum Punkte $0:0:1:i:0$ von G_3, so dass man noch eine vierte Isotrope so erhält:

$$G_4;\quad \lambda:0:\mu:i\mu:-\lambda$$

Zwei windschiefe Isotropen können immer durch eine einzige nicht spezielle Kugel verbunden werden. So ergeben sich hier die Verbindungskugeln von G_1G_3 und G_2G_3:

$$K_1;\quad -x_1+x_3-ix_2=0, \qquad K_2;\quad +x_1+x_3-ix_2=0.$$

Sie berühren sich längs aller Punkte von G_3 und von G_4; der Berührungspunkt ist also der Schnittpunkt (nicht von G_1 und G_2, sondern) von G_3 und G_4,

In dem Kugelbüschel von den Basiskugeln K_1 und K_2 tritt eine einzige spezielle Kugel K_3 auf; als K_4 bezeichnen wir ferner die Kugel, die im Kugelbüschel von K_3 harmonisch durch die Kugeln K_1 und K_2 getrennt wird:

$$K_3;\quad x_3-ix_2=0, \qquad K_4;\quad x_1=0.$$

Dann verhalten sich die Punkte der beiden Kugeln K_3 und K_4 singulär gegenüber der Transformation, wie wir sehen werden.

8. Jetzt stellen wir die Transformationsformeln auf. Zum Punkte x sind auf den Isotropen G_1, G_2, G_3 parallel[1]) die Punkte

$$\begin{array}{lllll} x_1+ix_2: & x_0+x_4: & i(x_0+x_4): & 0 & :-(x_1+ix_2), \\ x_1-ix_2: & x_0+x_4: & -i(x_0+x_4): & 0 & :-(x_1-ix_2), \\ x_2+ix_3: & 0 \quad : & x_0-x_4 \;: & i(x_0-x_4): & x_2+ix_3\,, \end{array}$$

und der dem Punkte x involutorisch zugeordnete Punkte y ist durch die drei Bedingungen

$$\left.\begin{array}{r} x_0y_1-x_1y_0-(x_1y_4-x_4y_1)=0, \\ x_0y_2-x_2y_0-(x_2y_4-x_4y_2)=0, \\ x_0y_2-x_2y_0+i(x_0y_3-x_3y_0)+(x_2y_4-x_4y_2)+i(x_3y_4-x_4y_3)=0 \end{array}\right\} \qquad (1)$$

bestimmt, zu denen noch

$$y_0^2-y_1^2-y_2^2-y_3^2-y_4^2=0$$

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[1]) Die Punkte x und y sind parallel, wenn $x_0y_0-x_1y_1-x_2y_2-x_3y_3-x_4y_4=0$.

kommt. Auf diese Weise erhalten wir die Transformationsformeln, die sich wohl am übersichtlichsten so schreiben lassen:

$$\left.\begin{aligned} y_0 + y_4 &= (x_3 - ix_2)^2 \,.\, (x_0 + x_4) \\ y_0 - y_4 &= x_1^2 \,.\, (x_0 - x_4) \\ y_1 &= (x_3 - ix_2)^2 \,.\, x_1 \\ y_2 &= (x_3 - ix_2)^2 \,.\, x_2 \\ y_3 - iy_2 &= x_1^2 \,.\, (x_3 - ix_2). \end{aligned}\right\} \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (2)$$

Danach ist die Transformation von dritter Ordnung, d.i. sie verwandelt eine Kugel im allgemeinen in eine Fläche, die von einer *Isotropen* in drei Punkten geschnitten wird. Eine Isotrope wird in eine Kurve dritter Ordnung übergeführt, wieder im Sinne der konformen Geometrie, d.i. in eine sphärische Kurve (wieder nur im allgemeinen).

9. Für die Punkte der beiden Isotropen G_3 und G_4 wird die Transformation *völlig* unbestimmt, für die sonstigen Punkte der Kugel K_3 insofern singulär, als sie sämtlich auf den Schnittpunkt von G_1 und G_2 geworfen werden. Alle übrigen Punkte der Kugel K_4 bilden sich auf die Punkte von G_3 ab.

Liegt der Punkt x auf keiner der beiden Kugeln K_3 und K_4, so verhält sich die Transformation regulär; Ruhepunkte (Fixpunkte) sind die Punkte der beiden Kugeln K_1 und K_2, natürlich nur diejenigen, die weder auf G_3 noch auf G_4 liegen.

In rechtwinkligen Kartesischen Koordinaten heisst die Transformation so:

$$\xi' = \xi, \qquad \eta' = \eta, \qquad \zeta' = \{\xi^2 + \eta^2 + i\eta\zeta\} : \{-\, i\eta + \zeta\},$$

wo der transformierte Punkt durch (ξ', η', ζ') bezeichnet ist.

10. Der Gestalt (1) unserer Transformation lässt sich eine neue Seite abgewinnen. Denn die drei Gleichungen (1) sind linear in den Grassmannschen Koordinaten

$$X_{jt} = x_j y_t - x_t y_j \,, \qquad (j, \quad t = 0, 1, 2, 3, 4)$$

der Verbindungsgeraden im R_4 der beiden Punkte x und y; man kann also schreiben

$$X_{01} - X_{14} = 0, \qquad X_{02} - X_{24} = 0, \qquad X_{12} = 0\,; \quad . \quad . \quad . \quad (3)$$

Die letzte Gleichung ergibt sich am bequemsten aus (2); sie ist eine Folge der fünf zwischen den X_{jt} bestehenden quadratischen Identitäten.

Eine solche lineare Gleichung in den X_{jt} ergibt eine Figur von ∞^5 geraden Linien des R_4, einen *Geradenpentakomplex*[1]; durch einen Punkt des R_4 laufen ∞^2, im Sonderfalle sogar ∞^3, gerade Linien des Komplexes.

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[1] CASTELNUOVO, Richerche di geometria della retta nello spazio a quattro dimensioni. Ven. Ist. Atti 7 (II); HOFFMANN, Die Nullsysteme im vierdimensionalen Raum. Diss. Bonn, 1928.

Drei solcher Geradenpentakomplexe, wie sie in (3) vorliegen, bestimmen ein Bündel, und der Durchschnitt aller Geradenpentakomplexe des Bündels ist ein *Geradentrikomplex*. Durch einen Punkt des R_4 allgemeiner Lage läuft eine einzige Gerade des Trikomplexes. Liegt sie nicht ganz auf M_3^2, so schneidet sie M_3^2 in zwei Punkten, und diese sind involutorisch zugeordnet.

11. Da ein Geradenpentakomplex durch ein Nullsystem (Punkt → Nullraum) des vierdimensionalen Raumes bestimmt wird — er besteht aus allen geraden Linien durch einen Punkt in seinem Nullraume — so lässt sich jetzt folgende viel allgemeinere Konstruktion einer involutorischen Punkttransformation des konformen Raumes angeben:

Man nimmt drei linear unabhängige Nullsysteme (Punkt → Nullraum) *im* R_4 *und bringt die* ∞^3 *gemeinsamen Nullgeraden* (bezw. *einen irreduziblen Bestandteil dieser Figur*) *mit* $M_3{}^2$ *zum Schnitt.*

Schon gegenüber projektiven Punkttransformationen des R_4 gibt es siebzehn verschiedene Typen solcher Tripel von Nullsystemen, und diese Zahl erhöht sich noch beträchtlich, wenn man gegenüber der Gruppe der automorphen Kollineationen der $M_3{}^2$ klassifiziert.

Diese Erklärung hat den Übelstand, dass sie nicht auf $M_3{}^2$ arbeitet, sondern auch im R_4. Im konformen Raum erscheint das Nullsystem von R_4 als Korrelation Punkt → Kugel, und die Geraden des Pentakomplexes, die auf $M_3{}^2$ liegen, finden sich wieder als die (isotropen) Tangenten der Minimalkurven einer Schar auf einer Dupinsche Zyklide, wenigstens im allgemeinen der acht Fälle [1]). Man müsste im konformen Raum also sagen:

Man nimmt drei linear unabhängige Kugelnullsysteme und bringt die drei Nullkugeln eines Punktes x zum Schnitt; der zweite Schnittpunkt y ist dem Punkte x involutorisch zugeordnet.

12. Und jetzt ergibt sicht leicht die Verallgemeinerung des Verfahrens von Herrn J. DE VRIES,

Man nimmt vier linear unabhängige Nullsysteme des R_5. *Jedes von ihnen bestimmt einen Heptakomplex von Nullgeraden des* R_5, *und der Durchschnitt aller dieser vier Heptakomplexe ergibt einen Tetrakomplex von Geraden des* R_5. *Diesen bringt man mit* $M_4{}^2$ *zum Schnitt.*

Ob es noch andere involutorische Geradentransformationen des dreidimensionalen projektiven Kontinuums gibt, hängt davon ab, ob es im R_5 Geradentetrakomplexe von der Ordnung 1 gibt, die nicht als Schnittfiguren von vier Nullsystemen erhalten werden können.

Bonn, den 30 März 1929.

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[1]) BÖHRES, Ueber zweigliedrige Gruppen konformer Transformationen des Raumes. Diss. Bonn, 1929.

Mathematics. — *Ueber das vierfach unendliche System der biquadratischen Raumkurven erster Art, welche durch vier gegebene Punkte gehen, zwei gegebene Geraden je einmal und eine dritte gegebene Gerade zweimal treffen.* By J. W. A. VAN KOL. (Communicated by Prof. HENDRIK DE VRIES).

(Communicated at the meeting of March 23, 1929).

§ 1. Eine Abbildung des vierfach unendlichen Systems der biquadratischen Raumkurven k^4 erster Art, welche durch vier gegebene Punkte $A_1, \ldots, A_4$ gehen, eine gegebene Gerade a zweimal und zwei gegebene Geraden a_1 und a_2 je einmal treffen, auf einen linearen vierdimensionalen Punktraum R_4 erhalten wir in folgender Weise. Es seien in R_4 α_1 und α_2 zwei beliebige Ebenen und Ω^2 ein quadratischer Raum mit einer Doppelgerade d. Wir beziehen die Punktreihe der Gerade a_1 projektiv auf den Büschel von linearen dreidimensionalen Punkträumen mit der Trägerebene α_i $(i = 1,2)$ und die Punktreihe der Gerade a projektiv auf das System der Tangentialräume von Ω^2. Einer Kurve k^4, welche a_1 in A'_1, a_2 in A'_2 und a in A' und A'' trifft, ordnen wir den Schnittpunkt der diesen Punkten zugeordneten Räumen zu. Diese Abbildung ist offenbar eineindeutig.

§ 2. *d ist eine Hauptgerade; ein beliebiger Punkt P von d ist das Bild des Systems der ∞^2 Kurven k^4, welche durch die den Räumen $P\alpha_1$ und $P\alpha_2$ zugeordneten Punkte von a_1 bzw. a_2 gehen und auf der Fläche zweiter Ordnung liegen, welche diese zwei Punkte und $A_1, \ldots, A_4$ und a enthält; die ∞^3 Kurven k^4, welche ihr Bild auf d haben, treffen a_1 und a_2 in entsprechenden Punkten einer projektiven Verwandschaft V.*

α_1 und α_2 sind singuläre Ebenen; ein beliebiger Punkt P von α_1 z.B. ist das Bild des Systems der ∞^1 Kurven k^4, welche durch die Punkte von a gehen, die den durch P gehenden Tangentialräumen von Ω^2 entsprechen, und zugleich durch den Punkt von a_2, der dem Raum $P\alpha_2$ entspricht; diese Kurven bilden eine Fläche vierter Ordnung mit Doppelpunkten in den eben genannten Punkten von a und a_2 und in $A_1, \ldots, A_4$.

Der Hauptpunkt $\alpha_1 \alpha_2$ ist das Bild des Systems der ∞^2 Kurven k^4, welche durch die Punkte von a gehen, die den durch $\alpha_1 \alpha_2$ gehenden Tangentialräumen von Ω^2 entsprechen.

Es gibt ∞^1 Gruppen von acht assoziierten Punkten, von denen vier in $A_1, \ldots, A_4$, zwei auf a, einer auf a_1 und einer auf a_2 liegen. Eine Gruppe von acht assoziierten Punkten hat die Eigenschaft, dasz die kubische Raumkurve, welche durch sechs dieser Punkte geht, die Gerade, welche durch die zwei übrigen Punkte geht, zweimal trifft. Die Folge ist, dasz jede der vier kubischen Raumkurven, welche durch $A_1, \ldots, A_4$ gehen und a zweimal und a_1 und a_2 je einmal treffen, auf a_1 und a_2 Punkte bestimmen, welche zu einer der erwähnten Gruppen assoziierter Punkte gehören. Es seien $P_{i\mu}$ $(i = 1, 2; \mu = 1, \ldots, 4)$ die Punkte, in denen diese Kurven $\overset{3}{k}_\mu$ a_i treffen. Die ∞^1 Gruppen assoziierter Punkte, zu denen P_1 und P_2 gehören, erzeugen auf a eine quadratische Involution I_μ. Dieser quadratischen Punkte-Involution ist eine quadratische Involution von Tangentialräumen von Ω^2 zugeordnet, welche die Eigenschaft hat, dasz die Ebene, welche zwei zugeordnete Räume gemein haben, in einem festen durch d gehenden Raum liegt. Die Gerade h_μ, welche dieser Raum und die P_1 und P_2 zugeordneten Räume gemein haben, ist offenbar die Bildgerade der ∞^1 Systeme von ∞^2 Kurven k^4, welche durch acht assoziierte Punkte gehen, von denen zwei in einem Punktepaar von I_μ und die übrigen in $A_1, \ldots, A_4$, $P_{1\mu}$ und $P_{2\mu}$ liegen.

Es gibt also vier Hauptgeraden h_μ, *welche* a_1 *und* a_2 *treffen; jeder Punkt von* h_μ *ist das Bild eines Systems von* ∞^2 *Kurven* k^4, *welche durch acht assoziierte Punkte gehen.*

§ 3. Jede Transversale von a_1, a_2 und d ist die Bildgerade einer Kurve k^4. Es gibt also ∞^2 singuläre Kurven k^4, welche a_1 und a_2 in entsprechenden Punkten von V treffen, Durch zwei beliebige Punkte von a geht eine singuläre Kurve k^4.

Die Ebene $(a_1 a_2) h_\mu$ bildet die entartete Kurve k^4 ab, welche aus $\overset{3}{k}_\mu$ und a besteht. Es gibt vier Kurven k^4, welche ∞^2 Bilder haben.

§ 4. Ω^2 ist der Bildraum des Systems der ∞^2 Kurven k^4, welche a berühren.

Betrachten wir das System Σ_1 der ∞^2 Kurven k^4, welche durch einen gegebenen Punkt P gehen. Wir bestimmen zunächst die Ordnung der Kurven, welche die Bildfläche O_P von Σ_1 mit a_1 und a_2 gemein hat. Es sei r eine Gerade, welche in a_1 und zugleich in einem Tangentialraum von Ω^2 liegt. Die Anzahl der Schnittpunkte van r und O_P ist gleich der Anzahl der Kurven von Σ_1, welche durch einen gegebenen Punkt A' von a gehen und überdies die Eigenschaft haben, dasz die Punkte, in denen sie a, auszer A', und a_2 treffen, einander in einer projektiven Verwandtschaft zwischen a und a_2 zugeordnet sind. Nun bilden die biquadratischen Raumkurven erster Art, welche durch sieben gegebene Punkte gehen und eine gegebene Gerade treffen, eine biquadratische Fläche mit Doppelpunkten in den gegebenen Punkten. Hieraus erhellt, dasz es vier Kurven von Σ_1 gibt, welche durch A' und einen zweiten gegebenen Punkt von a gehen und zwei Kurven von Σ_1, welche durch A' und einen gegebenen Punkt von a_2 gehen. Die oben gefragte Anzahl ist also sechs. Demnach hat O_P mit a_1 und a_2 Kurven sechster Ordnung gemein. Eine in a_1 durch den Punkt $a_1 a_2$ gelegte Gerade trifft

O_P auszer $\alpha_1 \alpha_2$ in zwei Punkten. Die Kurven sechster Ordnung haben also einen vierfachen Punkt in $\alpha_1\alpha_2$.

Auch O_P hat einen vierfachen Punkt in $\alpha_1 \alpha_2$; dieser Punkt ist ja das Bild der vier Kurven von Σ_1, welche durch die Punkte von a gehen, die den durch $\alpha_1 \alpha_2$ gehenden Tangentialräumen von Ω^2 zugeordnet sind.

Eine Ebene, welche mit α_1 und α_2 je eine Gerade gemein hat, hat mit O_P auszer α_1 und α_2 keinen Punkt gemein, da es im Allgemeinen keine biquadratische Raumkurve gibt, welche durch sieben gegebene Punkte geht und eine gegebene Gerade zweimal trifft. Hieraus erhellt, dasz O_P eine Fläche achter Ordnung ist.

Die Geraden h_μ sind einfache Geraden auf O_P und d liegt nicht auf O_P. Eine durch d gehende Ebene hat mit O_P auszer d vier Punkte gemein; d trifft also O_P in vier Punkten.

Die Eigenschaften von O_P fassen wir in folgender Weise zusammen:

Das System der Kurven k^4, welche durch einen gegebenen Punkt P gehen, wird abgebildet auf eine Fläche O_P achter Ordnung, welche einen vierfachen Punkt in $\alpha_1 \alpha_2$ hat, mit d vier Punkte gemein hat und mit α_i eine Kurve sechster Ordnung mit einem vierfachen Punkt in $\alpha_1 \alpha$ und einfachen Punkte in $\alpha_i h_\mu$ und auf welcher h_μ einfache Geraden sind.

Durch Anwendung eines Satzes von PIERI (siehe § 5) kann man beweisen, dasz zwei Flächen O_P und O_Q auszer singulären und Hauptpunkten vier Punkte gemein haben. Diese Punkte sind offenbar die Bilder der vier Kurven k^4, welche durch die gegebenen Punkte P und Q gehen und auf der Fläche zweiter Ordnung liegen, welche $A_1, \ldots, A_4$ P, Q und a enthält.

§ 5. Analog ist zu beweisen:

Das System der Kurven k^4, welche eine gegebene Doppelsekante b haben, wird abgebildet auf eine Fläche O_b neunter Ordnung, welche in $\alpha_1 \alpha_2$ einen vierfachen Punkt hat, mit h_μ einen Punkt und mit α_i eine Kurve sechster Ordnung mit einem vierfachen Punkt in $\alpha_1 \alpha_2$ gemein hat und auf welcher d eine einfache Gerade ist.

O_P und O_b haben auszer singulären und Hauptpunkten acht Punkte gemein.

Es gibt also acht Kurven k^4, welche durch einen gegebenen Punkt P gehen und eine gegebene Doppelsekante b haben.

Die Anzahl der Schnittpunkte von zwei Flächen O_{b_1} und O_{b_2}, welche auszer d liegen, bestimmen wir durch Anwendung eines Satzes von PIERI[1]), infolge dessen diese Anzahl gleich ist dem Produkt der Ordnungen von O_{b_1} und O_{b_2} vermindert um das Produkt der Vielfachheiten, mit denen d auf O_{b_1} und O_{b_2} liegt und um die Klasse des Raumes, der eingehüllt wird von den Räumen durch d, welche O_{b_1} und O_{b_2} in einem selben Punkt von d berühren. Diese Klasse bestimmen wir in folgender

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[1]) SIEHE: Rend. del Circolo Mat. di Palermo, 5, 1891.

Weise. Ein beliebiger Raum durch d hat mit O_{b_1} auszer d eine Kurve achter Ordnung gemein, welche d in vier Punkten trifft; dieser Raum berührt also O_{b_1} viermal, nämlich in den Schnittpunkten von d und der eben genannten Kurve achter Ordnung. Um zu bestimmen wieviel Räume durch d und einen beliebigen Punkt S O_{b_1} und O_{b_2} in einem selben Punkt von d berühren, ordnen wir einem beliebigen Punkt D von d die vier Punkte D' zu, in denen O_{b_2} berührt wird von dem Raum, der durch S und durch die Ebene geht, welche O_{b_1} in D berührt. Ebenfalls sind einem Punkte D' vier Punkte D zugeordnet. Die erhaltene viervierdeutige Verwandtschaft hat acht Koinzidenzen; die gefragte Klasse is also acht. O_{b_1} und O_{b_2} haben somit auszer d $9^2 - 1 - 8 = 72$ Punkte gemein, von denen 16 in $\alpha_1 \alpha_2$ und 2 (36—16) in α_1 und α_2 auszer $\alpha_1 \alpha_2$ liegen. Auszer singulären und Hauptpunkten haben O_{b_1} und O_{b_2} demnach 16 Punkte gemein.

Es gibt also 16 Kurven k^4, *welche zwei gegebene Doppelsekanten* b_1 *und* b_2 *haben.*

§ 6. Es sei Ω_l der Bildraum des Systems Σ_2 der ∞^3 Kurven k^4, welche eine gegebene Gerade l treffen. α_1 und α_2 sind vierfache Ebenen in Ω_l; denn es gibt vier Kurven von Σ_2, welche durch zwei gegebene Punkte von a und einen gegebenen Punkt von a_1 oder a_2 gehen. Es sei r eine Gerade, welche α_1 und α_2 trifft und in einem Tangentialraum von Ω^2 liegt. Die Anzahl der Punkte, welche r und Ω_l auszerhalb α_1 und α_2 gemein haben, ist gleich der Anzahl der Kurven von Σ_2, welche durch einen gegebenen Punkt von a, einen gegebenen Punkt von a_1 und einen gegebenen Punkt von a_2 gehen, also gleich zwei. Es ergibt sich somit, dasz Ω_l ein Raum zehnter Ordnung ist. Die Geraden d und h_μ sind Doppelgeraden in Ω_l (§ 7).

Das System der Kurven k^4, *welche eine gegebene Gerade 1 treffen, wird also abgebildet auf einen Raum* Ω_l *zehnter Ordnang, der in* $\alpha_1 \alpha_2$ *einen achtfachen Punkt hat und in dem* α_i *vierfache Ebenen und* d *und* h_μ *Doppelgeraden sind.*

§ 7. Zwei Räume Ω_l und Ω_m haben auszer α_1 und α_2 eine Fläche O_{lm} 68. Ordnung gemein. O_{lm} ist offenbar die Bildfläche des Systems der ∞^2 Kurven k^4, welche zwei gegebene Geraden l und m treffen. Die Eigenschaften von O_{lm}, welche man ableiten kann, indem man u.A. die Eigenschaft anwendet, dasz die biquadratischen Raumkurven erster Art, welche durch sechs gegebene Punkte gehen und drei gegebene Geraden schneiden, eine Fläche 32. Ordnung bilden mit 16-fachen Punkten in den gegebenen Punkten[1]), fassen wir in folgender Weise zusammen:

Das System der Kurven k^4, *welche zwei gegebene Geraden* l *und* m

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[1]) SIEHE: Der Komplex der biquadratischen Raumkurven erster Art, welche durch fünf gegebene Punkte gehen und drei gegebene Geraden schneiden, Nieuw Archief v. Wisk. **16**, S. 91.

treffen, wird abgebildet auf eine Fläche 68. Ordnung, welche in $\alpha_1 \alpha_2$ *einen 32-fachen Punkt hat, mit* α_i *eine Kurve 48. Ordnung mit einem 32-fachen Punkt in* $\alpha_1 \alpha_2$ *und vierfachen Punkten in* $\alpha_i h_\mu$ *gemein hat und auf welcher* d *und* h_μ *vierfache Geraden sind.*

Eine Folge der letzten Eigenschaft ist, dasz d und h_μ Doppelgeraden in Ω_l sind.

§ 8. Eine Fläche O_{lm} und ein Raum Ω_n haben auszer den Geraden d und h_μ und Kurven in α_1 und α_2 eine Kurve k_{lmn} 256. Ordnung gemein, welche offenbar die Bildkurve ist des Systems Σ_3 der Kurven k^4, welche drei gegebene Geraden l, m und n treffen. k_{lmn} hat mit α_1 und α_2 je $256 - 48 = 208$ Punkte gemein, weil es 48 Kurven von Σ_3 gibt, welche durch einen gegebenen Punkt von a_1 oder a_2 gehen (§ 9). Die biquadratischen Raumkurven erster Art, welche durch sechs gegebene Punkte gehen und fünf gegebene Geraden treffen, bilden eine Fläche 320. Ordnung mit 160-fachen Punkten in den gegebenen Punkten.[1]) Daraus folgt, dasz ein Tangentialraum von Ω^2 mit k_{lmn} auszer d 160 Punkte gemein hat und dasz also k_{lmn} 96 Punkte mit d gemein hat.

Die biquadratischen Raumkurven erster Art, welche durch $A_1, \ldots, A_4$, $P_{1\mu}$ und $P_{2\mu}$ gehen und l, m und n treffen, bilden eine Fläche 32. Ordnung, welche mit a 32 Punkte gemein hat, von denen je zwei auf einer Kurve von Σ_3 liegen, welche durch $P_{1\mu}$ und $P_{2\mu}$ geht. Die Anzahl dieser Kurven ist also 16. k_{lmn} hat demnach mit den Geraden h_μ je 16 Punkte gemein.

Das System der Kurven k^4, *welche drei gegebene Geraden* l, m *und* n *treffen, wird somit abgebildet auf eine Kurve* k_{lmn} *256. Ordnung, welche mit* d *96, mit* α_i *208 und mit* h_μ *16 Punkte gemein hat.*

k_{lmn} trifft Ω_o auszer singulären und Hauptpunkten in 576 Punkten.

Es gibt also 576 Kurven k^4, *welche vier gegebene Geraden* l, m, n *und* o *treffen.*

Auch Anwendung des Satzes von PIERI (§ 5) auf O_{lm} und O_{no} gibt diese Anzahl.

§ 9. In ähnlicher Weise lassen sich die Abbildungen von vielen anderen Systemen untersuchen, z. B. von den Systemen der Kurven k^4, welche i gegebene Gerade treffen und k gegebene Ebenen berühren ($i, k = 0, \ldots, 3$; $0 < i + k \leqq 3$); welche a_1 zweimal treffen und überdies 0,1 oder 2 gegebene Geraden einmal treffen; welche a_1 und a_2 je zweimal treffen. Für diese Untersuchungen braucht man einige Anzahlen, welche vom Verfasser schon abgeleitet sind, wie z. B. $P^7 \nu \varrho = 12$ und $P^7 \varrho^2 = 36$ [2]), $P^6 \nu^2 \varrho^2 = 288$ und $P^6 B \varrho^2 = 36$ [3]), und $P^5 B \nu \varrho^3 = 1296$ [4]).

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[1]) SIEHE: Nieuw Archief v. Wisk. **16**, S. 92.

[2]) Nieuw Archief v. Wisk., **16**, S. 86 und 94.

[3]) These Proceedings, **32**, 1.

[4] These Proceedings **31**, 9.

Die Anzahlen, welche sich hieraus berechnen lassen, und die oben berechneten Anzahlen sind:

$$\begin{array}{lllll}
P^5B^3=1 & P^6B\nu^2=4 & P^5B^2\nu^2=8 & P^5B\nu^4=48 & P^4B^3\nu^2=16 \\
P^4B^4=3 & & P^5B^2\nu\varrho=24 & P^5B\nu^3\varrho=144 & P^4B^3\nu\varrho=48 \\
 & & & P^5B\nu^2\varrho^2=432 & P^4B^3\varrho^2=144
\end{array}$$

$$\begin{array}{ll}
P^4B^2\nu^4=96 & P^4B\nu^6=576 \\
P^4B^2\nu^3\varrho=288 & P^4B\nu^5\varrho=1728 \\
P^4B^2\nu^2\varrho^2=864 & P^4B\nu^4\varrho^2=5184 \\
P^4B^2\nu\varrho^3=2592 & P^4B\nu^3\varrho^3=15552 \\
 & P^4B\nu^2\varrho^4=46656
\end{array}$$

$$\begin{array}{llll}
P^5T\nu^3=32 & P^4B^2T\nu=8 & P^4BT\nu^3=48 & P^4T\nu^5=320 \\
P^5T\nu^2\varrho=96 & P^4B^2T\varrho=24 & P^4BT\nu^2\varrho=144 & P^4T\nu^4\varrho=960 \\
 & & P^4BT\nu\varrho^2=432 & P^4T\nu^3\varrho^2=2880 \\
 & & & P^4T\nu^2\varrho^3=8640
\end{array}$$

P bedeutet die Bedingung, dasz eine biquadratische Raumkurve erster Art durch einen gegebenen Punkt gehen soll, B die Bedingung, dasz sie eine gegebene Doppelsekante haben soll, ν die Bedingung, dasz sie eine gegebene Gerade treffen soll, T die Bedingung, dasz sie eine gegebene Gerade berühren soll und ϱ die Bedingung, dasz sie eine gegebene Ebene berühren soll.

Chemistry. — *On the Behaviour of amorphous Carbon and Sulphur, compared with the Behaviour of Diamond and of Graphite and on the Carbonsulphide of* CIUSA. By J. P. WIBAUT and E. J. VAN DER KAM. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated at the meeting of April 28, 1928).

§ 1. *Introduction.*

In previous investigations [1]) on this subject has been shown that by heating mixtures of pure amorphous carbon and sulphur at 500—600° C. in sealed tubes, "sulphurous carbons" are formed which contain 15—25 % sulphur and which show the same appearance as the amorphous carbon before the treatment. When these substances were heated at 600° C. in a vacuum, about 50 % of the combined sulphur was splitted off, at higher temperatures still more of the sulphur separated, but finally, after heating at 1000—1100°, there result sulphurous carbons which still contain 2—3 % sulphur. If these substances are exposed to the action of gaseous hydrogen at 500—700°, nearly the whole quantity of fixed sulphur is eliminated as sulphide of hydrogen.

The experimental results led us to the conception that at least the strongly held sulphur in this sulphurous carbons is fixed to the carbon by valency forces. However, since WIBAUT and LA BASTIDE [2]) did not succeed in isolating any carbon-sulphur compound of definite composition from this sulphurous carbons (except carbondisulphide), it could not be decided if there were present in this sulphurous carbons one or more carbonsulphides of definite composition. It should be possible to settle this question if the pressure of the sulphur vapour above such substances could be measured at a constant temperature for varying compositions of the solid phase.

Before starting experiments on these lines, we thought it advisable to investigate a carbonsulphide in which the sulphur atoms are doubtless bound by primary valency forces. CIUSA [3]) obtained by decomposition of tetra-iodothiophen a black, carbonlike substance, which he called thiophen graphite, and to which the formula $(C_4S)_x$ was ascribed.

We have not been able to prepare a substance of the composition C_4S by this method ; the sulphur content of our preparations was too low and there was always a small content of iodine. An approximate estimation of the pression of the sulphur vapour above such a specimen at 500° was made with a glass-spring manometer ; the vapour pressure was between 5 and

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[1]) Rec. des trav. chim. des Pays-Bas **41**, 154 (1922); these Proceedings Vol. **24**, 92 (1921).

[2]) Rec. des trav. chim. des Pays-Bas **43**, 731 (1924).

[3]) Gazz. chim. **55**, 384 (1925).

7 cm mercury, an exact estimation was impossible as it was very difficult to eliminate absorbed gases from these substances, without simultaneously eliminating a part of the fixed sulphur. In view of this experimental difficulties the plan of making an extensive investigation of the vapour pressure of our sulphurous carbons, was given up.

Another point of interest was to make experiments with the cristalline modifications of carbon : diamond and graphite.

In a diamond crystal the valencies of the carbon atoms are completely saturated. If the fixation of sulphur by amorphous carbon is caused by unsaturated valencies of the carbon, it was to be expected that diamond powder should not be able to combine with sulphur. It may be said at once that we found that pure finely powdered diamond did not fix any sulphur at 500° or at 600°. Nor did highly purified Ceylon graphite fix any sulphur at 600°.

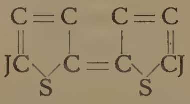
On the other hand we have found considerable differences in the quantities of sulphur fixed by different kind of amorphous carbon. We will first give a description of the experiments and afterwards a discussion of the results.

EXPERIMENTAL PART.

§ 2. *Preparation of sulphurous carbons.*

I. *From tetraiodothiophen according to* Ciusa.

Ciusa (3) heated tetraiodothiophen in a sealed tube at 340° ; iodine was liberated and a black, carbonlike substance resulted containing iodine and sulphur in the atomic ratio 1 : 1. For this reason Ciusa ascribes to this amorphous substance the formula



When this substance was heated in a current of carbon dioxyde "at beginning red heat" the iodine was split off and an amorphous substance resulted, thiophengraphite ; Ciusa found for the composition of this substance 37.57 % S and 54.71 % C. (C_4S requires 40 % S and 60 % C.).

We did not succeed in preparing a substance of the empirical composition C_4S notwithstanding several modifications in the mode of heating of the tetraiodothiophen were tried. In our experiments not only iodine but also sulphur was splitt off. The best result was obtained in the following manner : 5 grams tetraiodothiophen were put in a glass tube which was evacuated and then sealed off ; the glass tube was heated during 8 hours at 400° in an electrical furnace. The liberated iodine was removed from the reaction product by extraction with carbon tetrachloride ; the resulting black powder was put again in a glass tube, together with a spiral of silver wire. The tube after having been evacuated and sealed off, was heated at 400° (± 10°) during thirty days without interruption. The resulting product was again extracted with carbontetrachloride and dried. In this manner two preparations were obtained, black amorphous powders, which will be indicated by the letters T_1 and T_2.

Analysis	T_1 :	28.4 % S ;	2.9 % J
	T_2 :	31.3 % S ;	1.7 % J

Though the composition of this substances differs widely from the values calculated for C_4S, we have used them for several experiments, as it may be assumed that in these preparations the sulphur is fixed by chemical bounds to the carbon atoms.

II. *From amorphous carbon and sulphur.*

The amorphous carbon was prepared by heating previously outgassed sugar carbon in a vacuum at 1000° as described by WIBAUT and LA BASTIDE (l.c.) (anal.: 0.22 % ash, C 99.55 %, 99.76 %; H 0.40 %, 0.48 %).

Samples of 5 grams of this carbon were mixed with 5 grams finely powdered sulphur and the mixture was heated in sealed glass tubes at a constant temperature in the manner described in the paper just quoted. When the heating was finished the content of the tube was extracted during 7—10 days with boiling toluene, till no more sulphur was dissolved by the toluene. The resulting amorphous powders, which had the appearance of the original amorphous carbon were analysed and used for several experiments [1]). In table 1, the amorphous carbon which served for the preparations is indicated by the letter C and the sulpurous carbons which were obtained from it by the letters C_1, C_2, C_3 and C_4.

III. *From activated amorphous carbon and sulphur.*

The activated carbon was prepared by heating lumps of sugar charcoal at 900—960° with limited supply of air according to BARTELL and MILLER [2]). The activated carbon had a black velvety appearance. (Analysis: C 98.9 %, H 0.3 %, ash 0.31 % ; the ash contained no ferric oxyde).

As the activated carbon is very hygroscopic it was necessary to dry the sample by heating at 1000°, immediately before use ; the cooled sample was mixed as quickly as possible with sulphur and put in the reaction tube. Notwithstanding these precautions the tube, after being heated at 500°, contained some hydrogen sulphide, which was formed from water absorbed by the carbon sample. The tubes were therefore first heated at 500° during 24 hours, opened and sealed off again and afterwards heated at 600°.

In table 1 the sample of activated carbon is indicated by the letter A and the sulphurous carbons obtained from it by the letters A_1—A_4.

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[1]) The determination of the sulphur content of the sulphurous carbons described in § 2, I, II and III and in § 3 has been done by oxidising with nitric acid in a sealed tube according to CARIUS. All the analyses were done in duplicate.

[2]) Journ. Am. Chem. Soc. 44, 1866 (1922).

IV. *Experiments with diamond powder and sulphur.*

Diamond splitters, which are obtained as a by-product by the cleaving of diamonds were powdered in mechanically driven iron mortars ; a very fine white powder was obtained which contained 0.067 % of ash. We desire to express our thanks to Mr. J. van Zutphen from the "Diamantbewerkers Koperen Stelen Fonds", who very liberally put a sample of diamond powder at our disposition and to Mr. Quelle who supervised the preparation of the diamond powder in the laboratory of the institution just mentioned.

As for the experiments with diamond powder only small quantities were available, we have first tried an analytic method for determining the sulphur content of sulphurous carbons which was adopted to the use of small samples. The Carius method cannot be applied on diamond powder, more over the gravimetric determination of little quantities of barium sulfate is tedious. We have used the method of ter Meulen and Heslinga 1) in which the sample of substance is burned in moist oxygen, the sulphur dioxyde formed is absorbed by hydrogen peroxyde solution and the sulphuric acid titrated with $^1/_{50}$ n. natriumcarbonate. In adopting this method to the analysis of our sulphurous carbons, some precautions must be taken. We thank Prof. ter Meulen and Miss Ravenswaay for their kindly help and advice by this experiments.

The experiment with diamond powder was done as follows :

A mixture of 0.300 gram diamond powder and 0.300 gram sulphur was heated in a sealed tube during 24 hours at 500° ; when the cooled tube was opened, there was a very slight pressure. After sealing again the tube was heated during 24 hours at 600°. The contents of the tube were extracted twice with 100 ccm boiling toluene, the remaining diamond powder had quite the same appearance as the original sample. A sample was burned according the method just mentioned ; we did not find any sulphur, while a sulphur content of 0.2 % would have been detected with certainty.

V. *Experiments with Ceylon graphite.*

A sample of Ceylon graphite which had an ash content of 4.7 % was purified in the following manner.

The sample was successively treated with fused kalium hydroxyde, boiled with hydrochloric acid, heated in a current of dry chlorine at 500—600°, washed with distilled water, extracted with hot hydrofluoric acid, again washed and dried 2). After this treatment the sample consisted of small shining scales.

Analysis : ash 0.02 %, C 99.6 %, H 0.3 %.

A mixture of 5 grams of this graphite with 5 grams sulphur was heated first during 24 hours at 500° and then during 24 hours at 600°. After

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1) H. ter Meulen en J. Heslinga. Nieuwe methoden voor elementair analyse (Delft, 1925).

2) Cf. Dumas and Stas, Ann. Chim. et Phys. (3) **1**, 26 (1840).
Burns and Hulett, Journ. Am. Chem. Soc., **45** 574 (1923).

extracting the content of the tube as described before, the graphite was tested for sulphur by the method used in the experiments with diamond. There was no sulphur present in the graphite.

The results of the experiments with the carbon preparations C and A with diamond powder and graphite are compiled in table 1 :

TABLE 1.

Number of experiment	Preparation of carbon	Temperature and duration of heating	Sulphur content of sulphurous carbon (after extraction)
1	*C*	24 hours at 500° then 24 hours at 600°	C_1 19.4 %
2	*C*	24 hours at 500° then 24 hours at 600°	C_2 19.1 „
3	*C*	48 hours at 500°	C_3 14.7 „
4	*C*	48 hours at 350°	C_4 3.05 „
5	*A*	24 hours at 500° then 24 hours at 600°	A_1 9.8 „
6	*A*	24 hours at 500° then 24 hours at 600°	A_2 9.65 „
7	*A*	48 hours at 500°	A_3 9.5 „
8	*A*	48 hours at 350°	A_4 9.6 „
9	Diamond powder	24 hours at 500° then 24 hours at 600°	0 „
10	Graphite	24 hours at 500° then 24 hours at 600°	0 „

It will be seen from table 1 that the quantity of sulphur that is fixed, depends *ceteris paribus* on the properties of the carbon specimens. With purified sugar carbon (preparation C) the quantity of fixed sulphur varies with the temperature of heating ; the quantity of fixed sulphur at 350° is about $^1/_6$ of the quantity fixed at 600°. It may be remarked that the experiments at 600° show a very good concordance with the experiments described in the paper with La Bastide (l.c.) when one takes in mind that in these two investigations different samples of purified sugar carbon have been used.

The activated sugar carbon (preparation A) fixes much less sulphur than the carbon-preparation C ; it is remarkable that the quantity of sulphur fixed by this activated carbon seems to be independent of the temperature of heating between 350 and 600°.

It should be kept in mind that the influence of temperature alone on the phenomenon cannot be seen from these experiments, as in the experiments at 500° and 600° a different pressure of sulphur vapour prevailed in the sealed tubes.

§ 3. *Behaviour of the sulphurous carbons when heated in a vacuum.*

With the purpose of getting more information about the nature of the forces by which the sulphur is bound in the sulphurous carbons described in § 2, I, II, III, these substances were heated in a high vacuum at different temperatures, and the sulphur content of the remaining product was determined. A weighed quantity (1—6 grams) of sulphurous carbon was put in a porcelain boat, which was placed in a quartz tube near to the sealed bottom. The open end of the horizontal quartz tube was connected with two U-tubes provided with taps; the tubes were connected with a mercury diffusion pump and the apparatus was evacuated. When high vacuum prevailed in the apparatus, an electrical furnace, which had been heated previously on the desired temperature, was pushed over the quartz tube and the U-tubes were cooled in liquid air. In this manner the decomposition products were rapidly removed from the hot reaction tube, and the sulphur which was splitt off could not recombine with the carbon. The temperature was measured by means of a galvanometer and a thermocouple; the junction was kept at the outer wall of the quartz tube in front of the middle of the porcelain boat. Each heating experiment was continued during 6 hours (the temperature being kept constant at about 5°) while pumping continued and the U-tubes were kept in liquid air during the experiment. Then the furnace was removed from the quartz tube, and pumping and cooling of the U-tubes was continued till the quartz tube was at room temperature. The stop cocks of the U-tubes were closed and the tubes taken from the liquid air. The U-tubes were washed with dry ether and the etherical liquid tested with an etherical solution of triaethylphosphine; traces of carbondisulphide could be detected in this manner. Then the U-tubes were washed with carbon disulphide, and after evaporation of this liquid the remaining sulphur was weighed. The content of the porcelain boat, which always had the appearance of amorphous carbon was analysed. The quantity of combined sulphur in the carbon, augmented with the quantity of free sulphur found in the U-tubes corresponded approximatively with combined sulphur present in the original preparation; in these experiments only small quantities of carbondisulphide were formed, this substance was not estimated quantitatively.

In table 2 the results of this experiments are compiled. In the second column the letter and the original sulphur content of the sulphurous carbon which served for an experiment, is given. In the 3d, 4th and 5th column are given the sulphur contents of the sulphurous carbons which remained after heating at the indicated temperature. The sulphurous carbons in the 5th column are indicated by letters and indexes.

In experiment I the preparation C_1 containing 19.4 % sulphur was heated during 6 hours at 600° ; a part from the residue containing 6.5 % sulphur was heated at 800°, the sulphur content of the residue was then 4.8 % ; part of this residue was then heated at 1000°, after which a substance with 3.0 % sulphur remained. In experiments 2, 3, 4, 7 and 8 the sulphurous carbons were first heated at 600° during 6 hours ; without interrupting the experiment the temperature of the furnace was brought to 1000° and kept constant there for another period of 6 hours, the remaining sulphurous carbon was then analysed. In experiments 5 and 10 the substance was first heated at 600°, the residue analysed and parts of this residues heated at 1000°. In experiments 6 and 9 the substance was first heated at 800° during 6 hours, the residues were analysed and parts of it heated again at 1000°. After the heating at 1000° the *U*-tubes contained little quantities of carbondisulphide in all experiments (in N^{0}. 4 only traces). After the heating at 800° also carbondisulphide was found, but not after the heating at 600° in experiments 5 and 10 ; in experiment 1 where 6.2 gram of sulphurous carbon was used, a trace of carbondisulphide was formed after the heating at 600°. This is in accordance with our previous results, where we found that from a sulphurous carbon containing 21 % sulphur only traces of carbondisulphide were splitt off at 600°, while at 800° and 1000 ° some more of this substance was separated. (Compare WIBAUT and LA BASTIDE l.c.).

TABLE 2.

Number of experiment	Number and *S* content of sulphurous carbon	Sulphur content after heating in a high vacuum during 6 hours at:		
		600°	800°	1000°
1	C_1 19.4 %	6.5 %	C''_1 4.8 %	C'_1 3.0 %
2	C_2 19.1 „			C'_2 2.1 „
3	C_3 14.7 „			C'_3 2.7 „
4	C_4 3.05 „			C'_4 1.4 „
5	A_1 9.8 „	8.1 „		A'_1 4.6 „
6	A_2 9.65 „		6.1 %	A'_2 4.5 „
7	A_3 9.5 „			A'_3 4.3 „
8	A_4 9.6 „			A'_4 2.5 „
9	T_1 28.4 „ *S* 2.9 „ *J*		14.0 „ *S* 0.9 „ *J*	T'_1 4.8 „ *S* traces *J*
10	T_2 31.3 „ *S* 1.7 „ *J*	27.45 „ *S* 0.85 „ *J*		T'_2 5.2 „ *S* traces *J*

It is seen from table 2 that the greatest part of the sulphur from preparations C_1 is splitt off at 600° in a high vacuum, obviously this part of the sulphur is loosely bound ; a smaller part of the sulphur is firmly bound for after heating at 1000° in vacuum a carbon with 2—3 % sulphur results. On the other hand in the preparation T_2 (which has been prepared from tetraiodo-thiophen and wherein the sulphur atoms are beyond doubt bound in thiophen-rings), only a small proportion of the sulphur is split off at 600°. One might conclude that in preparation C_1 only a small part of the sulphur is fixed by primary valencies of the carbon atoms.

It is interesting that in the sulphurous carbon A_1, which is prepared from activated carbon and sulphur, the sulphur is firmly bound, only 17 % of the sulphur being separated at 600° in a vacuum.

Comparing the preparations A_1 and A_4 which have been prepared by heating activated carbon with sulphur at 600° and at 350° respectively, it is seen that the sulphur is more losely bound in A_4. Notwithstanding the activated carbon fixes the same quantities of sulphur when heated either at 600° or at 350°, it appears that the manner in which the sulphur is combined, is different in both cases.

§ 4. *The Action of hydrogen on the sulphurous carbons.*

It has been shown by POWELL[1]) and in our former papers (l.c.) that hydrogen reacts with sulphurous carbons at higher temperatures, whereby the sulphur is eliminated in the form of hydrogensuphide.

We have made comparative experiments with the sulphurous carbons described in § 2, on their behaviour towards hydrogen.

1500 cc hydrogen (15°, 760 mm) were passed at a constant rate over 0.350 gram of sulphurous carbon, which was heated at a constant temperature; the quantity of hydrogen sulphide in the outlet gases was determined. In table 3 are recorded the results of this experiments; the sulphurous carbons are indicated by the same letters as in tables 1 and 2.

TABLE 3. Action of hydrogen on sulphurous carbons at 400° C.

Number of experiment	Number and *S*-content of sulphurous carbon	Sulphur eliminated as H_2S in percentage of original sulphur
1	C_1 (19.4 % *S*)	22.8; 24.6
2	C_2 (19.1 „ *S*)	22.0; 23.8
3	A_1 (9.8 „ *S*)	2.6; 3.6
4	A_2 (9.65 „ *S*)	3.1; 3.7
5	T_1 (28.4 „ *S*)	9.5; 9.1
6	T_2 (31.3 „ *S*)	7.4
7	C_3 (14.7 „ *S*)	26.7
8	C_4 (3.05 „ *S*)	31.7
9	A_3 (9.5 „ *S*)	20.1
10	A_4 (9.6 „ *S*)	20.7; 21.9

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[1]) Journ. Amer. Chem. Soc. **45**, 1 (1923).

It is to be seen from table 3, that the results of duplicate experiments differ somewhat, but this differences are much smaller than the differences between different sulphurous carbons. It is obvious that these sulphurous carbons are attacked at different rates by hydrogen; *ceteris paribus* the sulphur is eliminated at a greater rate from the sulphurous carbons which are prepared from purified sugar carbon, then from those which are prepared from activated sugar carbon (compare experiment 1 and 2 with 3 and 4). The sulphurous carbons prepared from tetra-iodothiophen (T_1 and T_2) stand between the preparations just mentioned.

The sulphurous carbons which are prepared at 500° or at 350°, either from purified sugar carbon or from activated sugar carbon are more rapidly attacked by hydrogen than the sulphurous carbons which are prepared at 600° (compare exp. 7 and 8 with 1 and 2 or 9 and 10 with 3 and 4).

In another series of experiments we have exposed to the action of hydrogen at 600° the sulphurous carbons which had remained after the heating at 800° or at 1000° in vacuum. Preliminary experiments had shown that at 400° or at 500° only very small quantities of hydrogen sulphide were formed from this substances. In table 4 the results of the experiments are recorded (the numbers of the preparations are the same as in table 2).

TABLE 4. Action of hydrogen on sulphurous carbons at 600° C.

Number of experiment	Number and *S*-content of sulphurous carbon	Sulphur eliminated as H_2S in percentage of original sulphur
1	C''_1 (4.8 % *S*)	23.0; 22.7
2	A'_1 (4.6 „ *S*)	11.3
3	A'_2 (4.5 „ *S*)	12.8; 13.2
4	T'_1 (4.8 „ *S*)	10.2
5	T'_2 (5.2 „ *S*)	11.25
6	C'_4 (1.4 „ *S*)	10.7

5. *Discussion of the results.*

It follows from our experiments that only "amorphous carbons" are able to fix sulphur, while the cristalline modifications of carbon do not possess this property. It seems probable that at least a part of the sulphur in this sulphurous carbons is combined to the carbon-atoms by valency forces; these valency forces are therefore available in amorphous carbon, but not in diamond or graphite. This conclusion is in accord with recent views on the nature of amorphous carbon. DEBYE and SCHERRER [1]) concluded from an examination by X-rays that amorphous carbon was merely graphite in a powder form; this conclusion was supported by KOHLSCHÜTTER [1]) who founded his opinion on the chemical and physical properties of different species of graphite and amorphous carbons.

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[1]) Physik. Zeits. **18**, 301 (1917).

However RUFF, SCHMIDT and OLBRICH [2]) think that true amorphous carbons exist in which the atoms are not arranged in the graphite lattice, they concluded from their investigation of different kinds of amorphous carbon, that some of these varieties pass into graphite only at temperatures as high as 2000°. Their conclusion is that in typical amorphous carbons there exist at the surface (included the capillary surfaces) atoms the valency forces of which are not fully saturated by neighbouring atoms and which possess therefore "free valencies".

GARNER and MAC KIE [3]) point out that these surface atoms in such amorphous carbons may possess different degrees of unsaturation. The high value of the heat of adsorption for small amounts of adsorbed oxygen supports this idea.

RHEAD and WHEELER [4]) have shown in a very interesting investigation on the mode of combustion of carbon, that oxygen may be fixed by amorphous carbon at temperatures between 300° and 600°; according to these authors the fixed oxygen is present as a "loosely formed physico-chemical complex to which no definite formula can be assigned". As the temperature increases the fixed oxygen is released in the form of carbon monoxyde and carbon dioxyde. At a given temperature of decomposition only a part of the fixed oxygen is released; if the temperature increases another part of the fixed oxygen is split off in the form of oxydes of carbon.

It seems therefore that the forces by which the oxygen-atoms (or molecules) are held, are of different size; GARNER and MC KIE point out that this behaviour is to be expected with a truly amorphous substance, wherein surface-atoms of different energy-content occur.

Our sulphurous carbons show many analogies with the oxygenated carbons of RHEAD and WHEELER.

In the sulphurous carbons prepared from non activated amorphous carbon most of the sulphur is loosely bound; this is that part of the sulphur that is split off in a vacuum at 600°; another part however in still hold at 800° or even at 1000°. Obviously the forces by which the carbon-atoms are held in the sulphurous carbons of high sulphur content, are different in size. The same conclusion may be drawn from the splitting off of carbon-disulphide, which occurs over a range of temperatures.

That in our experiments most of the sulphur is liberated as free sulphur and not in the form of carbondisulphide, is in accordance with the fact that the affinity of carbon to sulphur is less than the affinity of carbon to oxygen. The fact that diamond powder and graphite are not capable to fix sulphur is in accordance with our hypothesis that this fixation is caused by unsaturated surface-atoms of the amorphous carbon ; in the cristalline modifications of carbon a comparatively small number of free valency forces in the surface is available, as compared with amorphous carbons.

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[1]) Zeits. anorg. Chem. **105**, 35 (1919).

[2]) Zeits. f. anorg. Chem. **148**, 313 (1925).

[3]) J. Chem. Soc., 1927, 2451.

[4]) J. Chem. Soc., **103**, 461 (1913).
C.f. LOWRY and HULETT, J. Am. Chem. Soc. **42**, 1408 (1920).

As the properties of an amorphous carbon may differ widely, according to different modes of preparation, it is quite conceivable that different carbons may show considerable quantitative differences in the behaviour towards sulphur, as we have found with the specimens of activated and non-activated sugar-carbon. However we are not able to explain why the influence of temperature on the phenomenon of sulphur fixation is so different for this two kinds of carbon.

In the sulphurous carbons which are prepared from tetraiodothiophen, the sulphur-atoms will beyond doubt form part of condensed thiophen-chains according to the supposition of CIUSA. It is interesting that the sulphur in this products is held more firmly than in the sulphurous carbons prepared from non-activated carbon, but less firmly than in those prepared from the activated carbon.

When these thiophen-carbons are heated at 1000° sulphurous carbons result, which show a close resemblance to the products prepared from activated carbon and sulphur after the same treatment (compare A_1' and A_2' with T_1' and T_2' in tables 2 and 4).

There seems no reason to suppose that in the sulphurous carbons T_1' and T_2' the sulphur-atoms are held only by surface-atoms. In this preparations there might be present a non volatible carbon-sulphide of low sulphur content, which seems a rather arbitrary hypothesis, or it might be supposed that the sulphur-atoms are dispersed in an irregular manner in the carbon lattice.

It would be interesting to investigate if there is a relation between the size of surface of different carbons and the quantity of sulphur that is fixed at a given temperature.

We express our thanks to Prof. Dr. A. SMITS who very kindly put at our disposition apparatus for vacuum work and a glass spring manometer, to Prof. H. TER MEULEN for his valuable help and advice in analytical difficulties and to Mr. J. VAN ZUTPHEN and Mr. J. QUELLE who put diamond-powder at our disposal.

Laboratory of organic Chemistry
of the University of Amsterdam.

March 1928.

Geology. — *Jurassic in the island of Sumba.* By P. M. ROGGEVEEN. (Communicated by Prof. L. RUTTEN.)

(Communicated at the meeting of September 29, 1928).

On an excursion through S.W. Sumba on the 8th of June 1910 H. WITKAMP [1]) found in campong Umbu Bewe a number of fossil lamellibranchs in sandy layers intercalated in a formation of shales.

Initially he supposed these fossils to be Inocerami. G. BOEHM [2]), however, who received the material from Utrecht for closer examination determined the fossils as Posidonomya Becheri Bronn, and on this ground advocated the probability of the occurrence of carboniferous in Sumba. But in the account of his excursion WITKAMP already says, that afterwards BOEHM was in doubt whether this determination was correct. WITKAMP supposes that the formation found by him must be referred to the Upper-Cretaceous. Also BROUWER [3]) and RUTTEN [4]) have pronounced their opinion that the deposit is presumably of young mesozoic age.

In 1912 WITKAMP presented the Mineralogical-Geological Institute at Utrecht with some more material from the same locality. The investigation of this material, so far unexamined, yielded some new results.

The rocks are dark-grey, more or less sandy shales, mostly somewhat effervescent with hydrochlorid acid. In some layers angular quartz-grains with a calcareous cement predominate.

Beyond the material which consisted chiefly of impressions, I encountered scanty remains of the shell of the lamellibranchs. These fragments are typical of the shell-structure of Inoceramus. The outer-layer, namely, is composed of rather large lime-prisms, normal to the shell-surface. Their dimensions slightly vary in various specimens, the greatest length and breadth being about 0,6 mm. and 0.15 mm. Similar, quite analogous shell-structures also presented other Inocerami, which were examined for comparison. Of the interior shell-layer thin remains without a distinct structure have been preserved here and there in the troughs between the ribs of the impressions.

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[1]) H. WITKAMP. Een verkenningstocht over het eiland Soemba. Tijdschr. Kon. Ned. Aardr. Gen. 2de serie XXIX, 1912, XXX, 1913, p. 17.

[2]) G. BOEHM. Posidonomya Becheri in Niederländisch-Indien? Zur Geologie des indo-australischen Archipels VII, Centralblatt f. Miner. Geol. u. Pal., 1911, p. 350—352.

[3]) H. A. BROUWER. Geologisch overzicht van het Oostelijk gedeelte van de Oost-Indische Archipel. Jaarboek Mijnwezen N. O. I., XLVI, 1917 (1919), Verhandelingen 2de gedeelte, p. 341.

[4]) L. M. R. RUTTEN. Voordrachten over de geologie van Nederlandsch Oost-Indië. Wolters, Groningen 1927, p. 668, 678.

As BOEHM has not given a specific description, I have considered it well to do so here. Our specimens (impressions) are about ten in number, but they are in part very fragmentary. (Vide fig. 1 and photo G. BOEHM 1911, after a cast of plaster).

The shell is oval-shaped, and little convex (the maximum thickness, measured vertically to the plane through the valve-borders, is about $^{3}/_{4}$ c.m. in the figured specimen). The long hinge-line is straight. On its fore-side we find the slightly curved umbo. The largest shell-length, measured parallel to the hinge-line lies at about the middle of the shell-height. The anterior border of the shell, and the hinge-line encompass an angle of ± 135°. The course of the concentric ribs is generally regular, a single one terminates on the valve. The ribs reach the hinge-line at angles of about 45°, their openings being turned from the umbo. Here the distances between the ribs are smaller than on the valve. In front the ribs run fairly into each other. The distances between the youngest ribs are the largest. The ribs are rather sharp, the troughs on the other hand are rounded. As for ligament-grooves and muscular impressions the available specimens do not admit of observation.

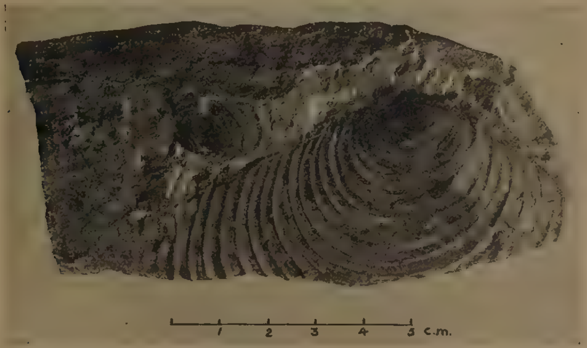

Fig. 1

The species above-described differs from the species of the genus Inoceramus, so far known from the Dutch-Indian Archipelago.

During the preparation of the lamellibranchs a few other fossils were disclosed, viz. some fish-toothlets and a fragment of an ammonite-shell. According to Prof. L. F. DE BEAUFORT the toothlets may appear to be those of a shark of the family Lamnidae.

The fragment of the ammonite-shell is of greater importance (fig. 2). It is a part of the exterior whorl of an Aegoceratid. The outer portion is provided with a rounded ridge bordered on either side by a shallow groove, lateral of which there occur ribs which gradually pass into nodules. Only in some places indistinct lines of growth may be observed.

Nothing is perceptible of suture lines, Dr. P. KRUIZINGA, who was so kind as to give his opinion about the fragment, deems it not quite impossible that it is a young Hammatoceras Molukkanum Cloos, described by him from the Jurassic of the Sula-islands.[1] However, considering the very fragmentary character of the remains, and the fact that the resemblance is not complete, it seems to me advisable not to give a specific determination. Together with the ammonite, remains of the Inoceramus occur in the same piece of rock. The age of the pretertiary of Umbu Bewe encountered by WITKAMP is established by the occurrence of the Aegoceratid as Jurassic.

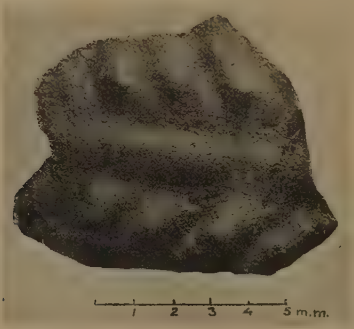

Fig. 2,

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[1] P. KRUIZINGA. Ammonieten en eenige andere fossielen uit de jurassische afzettingen der Soela Eilanden. Jaarboek Mijnwezen N. O. I., 1925 (1926), Verhandelingen 1ste gedeelte.

Physics. — *The* ZEEMAN*-effect in the spectrum of ionized Neon* (*Ne II*). By C. J. BAKKER. (Communicated by Prof. P. ZEEMAN.)

(Communicated at the meeting of November 24, 1928)

1. *Introduction.* In a former paper in these Proceedings ¹) the results of the experimental investigation of the ZEEMAN-effect in the spectrum of ionized Argon (*Ar II*) have been communicated. It appeared that different terms in the energy scheme of ionized Argon have „anomalous" *g*-values, which shows that there are deviations from the normal coupling scheme of RUSSELL-SAUNDERS. ²)

After this investigation on the coupling relations in the energy scheme of ionized Argon (*Ar II*) it was important to perform an analogous investigation concerning the spectra of the ionized atoms of the other inert gases, to get in this way a survey concerning the deviations dependent on the atomic number.

According to theoretical considerations one expects that the deviations for analogous terms increase with the atomic number. This paper gives the investigation of the ZEEMAN-effect in the spectrum of ionized Neon (*Ne II*) and is directly related to the investigations on spectra with and without magnetic field in the laboratory of Prof. ZEEMAN.

2. *Experimental part.* I can refer for the greater part to the communication on the ZEEMAN-effect of ionized Argon (*Ar II*), because for the investigation of ionized Neon (*Ne II*) the same method and mounting has been used. The Neon gas was led into a copper vacuum box enclosing the poles of the large magnet of the laboratory. The pressure of the Neon in the vacuum space must be 2 à 3 cm for getting brilliant discharges.

In connection with the small sputtering coefficient of Aluminium I used *Al* electrodes in the magnetic field. The longest times of exposure amounted to 6 hours; on account of the impurities, which come free with such discharges of long duration and which oppress the pure noble gas spectrum it was necessary to renew the Neon filling each $1^1/_2$ hour. I used an uncondensed high potential alternating current furnished by a large transformer. This discharging method in the magnetic field gives the spectrum of *Ne II* weaker than formerly the spectrum of *Ar II*.

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¹) C. J. BAKKER, T. L. DE BRUIN and P. ZEEMAN; These Proceedings **31**, 780, 1928. Zeitschr. f. Phys. **51**, 114, 1928; **52**, 299, 1928.

²) C. J. BAKKER: These Proceedings **31**, 1041, 1928.

This must be due to the higher ionization potential of *Ne I* (*Ne I* 21,5 Volt [1]) and *Ar I* 15,7 Volt [2]) and the higher excitation potentials of *Ne II*.

The largest strength of the magnetic field, attained during this investigation was 41400 ± 150 Gauss (diameter of the pole tips of the magnet 5 mm, distance ± 6 mm).

The exposures and measurements of the magnetic separations are made in the 2nd and 3rd order of a large 6 inch ROWLAND-grating mounted in the stigmatic grating mounting of the laboratory. Special attention is given to the constant temperature of the grating during the exposures (l.c. Argon *II*).

3. *Investigation and results.*

In the spectrum of ionized Argon (*Ar II*) the g-values of the term groups arising from the $4s$, $4p$ and $5s$ electron are investigated. The goal of the investigation here given has been to fix in the spectrum of ionized Neon (*Ne II*) the g-values arising from the $3s$, $3p$ and $4s$ electron. However the terms arising from the $4s$ electron are accessible only with difficulty for the investigation of the magnetic separation, because the spectral lines arising from these terms by combination with the $3p$ terms are weak lines of the spectrum (intensity < 4), lying in the neighbourhood of 3000 Å. Therefore I had to limit myself to the investigation of the $3s$ and $3p$ terms.

The coupling of a $3s$ electron with the atomic core of *Ne II* gives $3s\,{}^4P_{321}$ and $3s\,{}^2P_{21}$, the coupling of a $3p$ electron gives $3p\,{}^4D_{4321}$, $3p\,{}^4P_{321}$, $3p\,{}^4S_2$ and $3p\,{}^2D_{32}$, $3p\,{}^2P_{21}$, $3p\,{}^2S_1$. The quartet terms are known by the extensive analysis of the spectrum by DE BRUIN [3]), the doublet combinations are found by me by means of the ZEEMAN effect in agreement with the classification presumed by DE BRUIN and given by RUSSELL, COMPTON and BOYCE [4]).

In the following tables the ZEEMAN effect of the spectral lines is given after the multiplets in which those lines are classified.

In the 3rd column is:

L = ZEEMAN effect calculated with LANDÉ's g-formula.
obs. = observed ZEEMAN effect.
calc. = ZEEMAN effect calculated with anomalous g-values.

The last column refers to the theoretical g-values (theor.) calculated with LANDÉ's g-formula and to the g-values (obs.) calculated from the observed ZEEMAN effect.

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[1]) G. HERTZ: Zeitschr. f. Phys. **18**, 307, 1923; Naturw. **12**, 1211, 1924. G. HERTZ and R. K. KLOPPERS: Zeitschr. f. Phys. **31**, 463, 1925.

[2]) K. W. MEISSNER: Zeitschr. f. Phys. **37**, 238, 1926; **39**, 172, 1926; **40**, 839, 1927.

[3]) T. L. DE BRUIN: These Proceedings **31**, 2, 1928; **31**, 593, 1928. Zeitschr. f. Phys. **44**, 157, 1927; **46**, 856, 1928.

[4]) H. N. RUSSELL, K. T. COMPTON and J. C. BOYCE: Proc. Nat. Ac. of Sc. Am. **14**, 280, 1928.

Besides the magnetic separations given in the tables there are some more upon my plates (e.g. those of spectral lines which are combinations between the doublet terms of the $3p$ and $3d$ electron) I shall give those in a following communication.

As strong triplet there is in the first order the ZEEMAN effect of the strongest line of the arc spectrum of Neon $\lambda = 5852{,}487$ ($3s\,{}^1P_1 - 3p\,{}^3P_0$) I measured (0,00) $1{,}03^5$ which agrees very well with the measurement of BACK (0,00) 1,034 1).

The tables show that the doublet lines

3557.84 $3s\,{}^2P_1 - 3p\,{}^2S_1$
3481.93 $3s\,{}^2P_2 - 3p\,{}^2S_1$
and
3378.28 $3s\,{}^2P_1 - 3p\,{}^2P_1$
3309.78 $3s\,{}^2P_2 - 3p\,{}^2P_1$

have ZEEMAN effects that deviate from the ZEEMAN effect calculated with LANDÉ's g-formula. Thus we see that there are anomalous g-values here, which can be calculated from the observed ZEEMAN effect with

3p \ 3s	$^4P_1$	299.1	$^4P_2$	517.7	$^4P_3$
$^4P_1$	5. 3751.26 26650.2	299.0	7. 3709.643 26949.1		—
182.6					
$^4P_2$	8. 3777.162 26467.4	299.2	7. 3734.94 26766.6	517.6	9. 3664.089 27284.2
222.6					
$^4P_3$	—		8. 3766.286 26543.8	517.8	10. 3694.22 27061.6
$^4D_1$	5. 3344.43 29891.9	299.1	3. 3311.30 30191.0		—
144.1					
$^4D_2$	5. 3360.63 29747.8	299.2	5 3327.16 30047.0	517.9	2. 3270.79 30564.9
249.6					
$^4D_3$	—		7. 3355.05 29797.4	517.7	7. 3297.74 30315.1
337.2					
$^4D_4$	—		—		10. 3334.837 29977.8
$^4S_2$	4. 3028.85 33006.2	293.1	6. 3001.646 33305.3	517.4	7. 2955.735 33822.7

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1) E. BACK: Ann. der Phys. **76**, 817, 1925.

λ	Termcomb. x—y		ZEEMAN-effect	g_x		g_y	
				theor.	obs.	theor.	obs.
3777.162	3s $^4P_1$ — 3p $^4P_2$	L	**(0.47)** **1.26** 2.20				
		obs.	(0.46^5) **1.25** 2.19^5	2.67	2.67	1.73	1.7
3766.286	3s $^4P_2$ — 3p $^4P_3$	L	**(0.07)** (0.20) **1.40** 1.53 1.67 1.80				
		obs.	**(0.00)** **1.45**	1.73	1.73	1.60	1.6
3751.26	3s $^4P_1$ — 3p $^4P_1$	L	(0.00) 2.67				
		obs.	(0.00) 2.66^5	2.67	2.67	2.67	2.6
3734.94	3s $^4P_2$ — 3p $^4P_2$	L	(0.00) 1.73				
		obs.	(0.00) 1.72^5	1.73	1.73	1.73	1.7
3709.643	3s $^4P_2$ — 3p $^4P_1$	L	**(0.47)** **1.26** 2.20				
		obs.	**(0.46)** **1.26** 2.20	1.73	1.73	2.67	2.6
3694.22	3s $^4P_3$ — 3p $^4P_3$	L	(0.00) 1.60				
		obs.	(0.00) 1.60	1.60	1.60	1.60	1.6
3664.089	3s $^4P_3$ — 3p $^4P_2$	L	**(0.07)** (0.20) **1.40** 1.53 1.67 1.80				
		obs.	**(0.00)** **1.48**	1.60	1.60	1.73	1.7
3360.63	3s $^4P_1$ — 3p $^4D_2$	L	**0.47** **(0.73)** 1.93				
		obs.	**0.60**	2.67	2.67	1.20	1.2
3355.05	3s $^4P_2$ — 3p $^4D_3$	L	**(0.18)** (0.54) **0.83** 1.19 1.55 1.91^5				
		obs.	**(0.19)** **0.85**	1.73	1.73	1.37	1.3
3344.43	3s $^4P_1$ — 3p $^4D_1$	L	(1.33) 1.33				
		obs.	(1.33) 1.33	2.67	2.67	0.00	0.0
3334.837	3s $^4P_3$ — 3p $^4D_4$	L	**(0.09)** (0.26) (0.43) **1.00** 1.17 1.34 1:51 1.69 1.86				
		obs.	**(0.00)** **1.12**	1.60	1.60	1.43	1.4
3327.16	3s $^4P_2$ — 3p $^4D_2$	L	(0.27) **(0.80)** 0.93 **1.47** 2.00				
		obs.	**(0.78^5)** **1.48**	1.73	1.73	1.20	1.2
3297.74	3s $^4P_3$ — 3p $^4D_3$	L	(0.11) (0.34) **(0.57)** 1.03 1.26 **1.49** 1.71 1.94				
		obs.	**(0.51)** **1.51**	1.60	1.60	1.37	1.3

REMARKS.

1. Very sharp sextet. See photogram 2.
2. „Pseudotriplet''. Central component enlarged; in both the other large components decrease of intensity clearly to the outside.
3. Sharp, wide triplet.
4. Sharp triplet.
5. Very sharp sextet. See photogram 4.
6. Strong, sharp triplet. See photogram 5.
7. „Pseudotriplet'' just as 3766, 286 (3*s* $^4P_2$—3*p* $^4P_3$).
8. Weak diffuse doublet.
9. Weak, diffuse quartet.
10. Very sharp doublet. See photogram 9.
11. „Pseudotriplet''. Central component enlarged; in both the other large components decrease of intensity to the outside. See photogram 10.
12. Weak, diffuse quartet.
13. Weak, diffuse quartet.

3p \ 3s	$^2P_2$	612.5	$^2P_1$
$^2D_3$	10. 3713.089 26924.0		—
511.4			
$^2D_2$	5. 3643.89 27435.4	612.5	9. 3727.08 26822.9
$^2S_1$	6. 3481.93 28711.5	612.6	4. 3557.84 28098.9
$^2P_2$	7. 3323.74 30077.9	612.2	6. 3392.80 29465.7
126.8			
$^2P_1$	3. 3309.78 30204.8	612.5	5. 3378.28 29592.3

λ	Termcomb. x—y		ZEEMAN-effect	g_x theor.	g_x obs.	g_y theor.	g_y obs,	Remarks
3727.08	$3s\ ^2P_1 - 3p\ ^2D_2$	L obs.	(0.07) 0.73 **0.87** **(0.00)** **0.82^5**	0.67	0.67	0.80	0.80	1)
3713.089	$3s\ ^2P_2 - 3p\ ^2D_3$	L obs.	**(0.07)** (0.20) **1.00** 1.13 1.27 1.40 **(0.00)** **1.07**	1.33	1.33	1.40	1.40	2)
3643.89	$3s\ ^2P_2 - 3p\ ^2D_2$	L obs.	(0.27) 0.53 **(0.80)** **1.07** 1.60 **0.83^6**	1.33	1.33	1.40	1.40	3)
3557.84	$3s\ ^2P_1 - 3p\ ^2S_1$	L obs. calc.	(0.67) 1.33 (0.64) 1.32 (0.64^5) 1.31^5	0.67	0.67	2.00	1.96	4)
3481.93	$3s\ ^2P_2 - 3p\ ^2S_1$	L obs. calc.	1.67 **1.00** **(0.33)** **(0.33)** **1.00** 1.67 1.64 **1.02** **(0.29^5)** **(0.29^5)** **1.02** 1.61 1.64 **1.02** **(0.29)** **(0.29)** **1.02** 1.64	1.33	1.33	2.00	1.96	5)
3392.80	$3s\ ^2P_1 - 3p\ ^2P_1$	L obs.	**(0.33)** 1.00 **1.67** **(0.33^5)** 0.99^5 **1.66**	0.67	0.67	1.33	1.33	6)
3378.28	$3s\ ^2P_1 - 3p\ ^2P_2$	L obs. calc.	(0.00) 0.67 (0.00) 0.68^5 (0.02) 0.69	0.67	0.67	0.67	0.71	7)
3323.74	$3s\ ^2P_2 - 3p\ ^2P_2$	L obs.	(0.00) 1.33 (0.00) 1.33	1.33	1.33	1.33	1.33	8)
3309.78	$3s\ ^2P_2 - 3p\ ^2P_1$	L obs. calc.	**1.67** 1.00 **(0.33)** **(0.33)** 1.00 **1.67** **1.62^5** **(0.30^5)** **(0.30^5)** **1.64** **1.64^5** 1.02 **(0.31)** **(0.31)** 1.02 **1.64^5**	1.33	1.33	0.67	0.71	9)

REMARKS.

1. Somewhat diffuse triplet.
2. „Pseudotriplet". Central component enlarged; in both the other large components decrease of intensity to the outside. See photogram 3.
3. Weak, diffuse doublet. Decrease of intensity to the outside.
4. Very sharp quartet. See photogram 6.
5. Very sharp sextet. See photogram 7.
6. Very sharp sextet. See photogram 8.
7. Sharp triplet.
8. Sharp triplet.
9. Weak, sharp quartet.

the method as given for instance in our communication on the ZEEMAN effect of ionized Argon (*Ar II*) l.c.

The tables 3 and 4 contain the *g*-values calculated from LANDÉ's *g*-formula (g_L) and the observed *g*-values (g_{obs}) for the terms arising from the coupling of a 3*s* and 3*p* electron. The last column refers to the *g*-sums of LANDÉ. One must expect namely that in each of both tables 3 and 4 the sum of the *g*-values of the terms with the same inner quantum number *j* is equal to the sum of LANDÉ's *g*-values for these terms, also when the *g*-values of the separate terms deviate from those of LANDÉ. The terms of the 3*s* electron all have normal *g*-values. This agrees with what has been found for ionized Argon (*Ar II*), then the analogous terms arising from the 4*s* electron all have normal *g*-values. The *g*-sum rule is of course fulfilled.

Among the terms of the 3*p* electron both the terms $3p\,^2S_1$ and $3p\,^2P_1$ have anomalous *g*-values. The *g*-sum rule is fulfilled.

In connection with the anomalous *g*-values of the two 3*p* terms it is remarkable that in the spectrum of ionized Argon (*Ar II*) just the analogous terms of the 3*p* electron $4p\,^2S_1$ and $4p\,^2P_1$ are those which

TABLE 3. TERMS OF THE 3s-ELECTRON

		$^4P_3$	$^4P_2$	$^4P_1$	$^2P_2$	$^2P_1$	
j = 1	g_L			2.67		0.67	$\Sigma g_L = 3.34$
	$g_{obs.}$			2.67		0.67	$\Sigma g_{obs.} = 3.34$
j = 2	g_L		1.73		1.33		$\Sigma g_L = 3.06$
	$g_{obs.}$		1.73		1.33		$\Sigma g_{obs.} = 3.06$
j = 3	g_L	1.60					$\Sigma g_L = 1.60$
	$g_{obs.}$	1.60					$\Sigma g_{obs.} = 1.60$

TABLE 4. TERMS OF THE 3P-ELECTRON.

		$^4P_3$	$^4P_2$	$^4P_1$	$^4D_4$	$^4D_3$	$^4D_2$	$^4D_1$	$^2D_3$	$^2D_2$	$^4S_2$	$^2S_1$	$^2P_2$	$^2P_1$	
$j=1$	g_L			2.67				0.00				2.00		0.67	$\Sigma g_L = 5.34$
	$g_{obs.}$			2.67				0.00				1.96		0.71	$\Sigma g_{obs.} = 5.34$
$j=2$	g_L		1.73				1.20			0.80	2.00		1.33		$\Sigma g_L = 7.06$
	$g_{obs.}$		1.73				1.20			0.80	2.00*		1.33		$\Sigma g_{obs.} = 7.06$
$j=3$	g_L	1.60				1.37			1.20						$\Sigma g_L = 4.17$
	$g_{obs.}$	1.60				1.37			1.20						$\Sigma g_{obs.} = 4.17$
$j=4$	g_L				1.43										$\Sigma g_L = 1.43$
	$g_{obs.}$				1.43										$\Sigma g_{obs.} = 1.43$

*) Not experimentally fixed.

show in there g-values the largest deviations from the normal g-values of LANDÉ.

Table 5 shows that the deviation of the g-value of LANDÉ for those analogous terms of ionized Neon (*Ne II*) and ionized Argon (*Ar II*) goes in the same direction and increases from Neon (atomic number 10) to Argon (atomic number 18).

TABLE 5.

TERM Neon II $n=3$ Argon II $n=4$	g-values		
	LANDÉ	*Ne* II	*Ar* II
$np\ ^2P_1$	0.67	0.71	0.99
$np\ ^2S_1$	2.00	1.96	1.68

4. *Summary.*

The ZEEMAN effect of the spectrum of ionized Neon (*Ne II*) has been investigated. The g-values of the terms arising from the $3s$ and $3p$ electron are tested by the g-values of LANDÉ for these terms. Some anomalous g-values are found and compared with the g-values of the analogous terms in the energy scheme of ionized Argon (*Ar II*).

In conclusion the author wishes to express thanks to Prof. ZEEMAN for valuable advice and helpful suggestions.

Laboratory "Physica" University of
Amsterdam.

November, 1928.

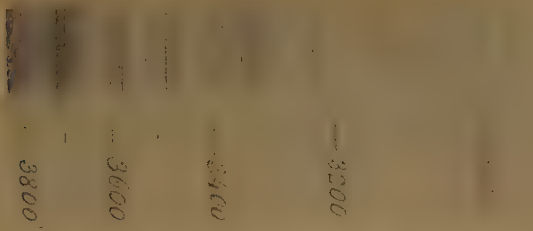
DESCRIPTION OF THE PLATE.

1. is an exposure with a Hilger quartz spectrograph (type *E* 3) and gives a survey of the investigated part of the spectrum of ionized Neon (*Ne II*), as it is excited by a discharge parallel the magnetic field of ± 41000 Gauss.

The photograms are made with a photometer (made by the firm of Zeiss), provided with photo-electric cell and electrometer.

2.	3777.162	$3s\,{}^4P_1 - 3p\,{}^4P_2$
3.	3713.089	$3s\,{}^2P_2 - 3p\,{}^2D_3$
4.	3709.643	$3s\,{}^4P_2 - 3p\,{}^4P_1$
5.	3694.22	$3s\,{}^4P_3 - 3p\,{}^4P_3$
6.	3557.84	$3s\,{}^2P_1 - 3p\,{}^2S_1$
7.	3481.93	$3s\,{}^2P_2 - 3p\,{}^2S_1$
8.	3392.80	$3s\,{}^2P_1 - 3p\,{}^2P_2$
9.	3344.43	$3s\,{}^4P_1 - 3p\,{}^4D_1$
10.	3334.837	$3s\,{}^4P_3 - 3p\,{}^4D_4$

C. J. BAKKER: THE ZEEMAN-EFFECT IN THE SPECTRUM OF IONIZED NEON (NE II).



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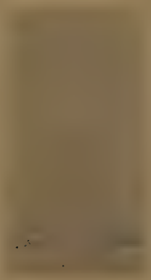

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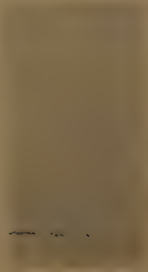

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10.

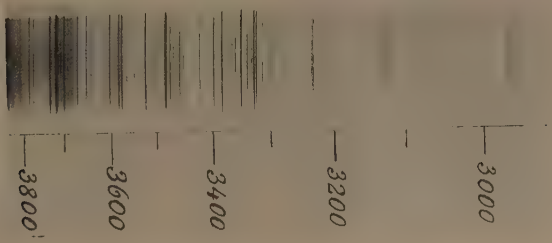
DESCRIPTION OF THE PLATES.

1. is an exposure with a HILGER quartz spectrograph (type E 3) and gives a survey of the investigated part of the spectrum of [illegible] Neon (Ne II), as it is excited by a discharge parallel the magnetic field of [illegible] Gauss.

The photograms are made with a [illegible] (made by the firm of ZEISS), provided with photo-electric cell and electrometer.

2.	3777.162	$3s\ {}^4P_1 - 3p\ {}^4P_2$	7.	3481.93	$3s\ {}^2P_2 - 3p\ {}^2S_1$
3.	3713.089	$3s$ [illegible]	8.	3392.80	$3s\ {}^2P_1 - 3p\ {}^2P_2$
4.	3709.643	$3s\ {}^4P_2 - 3p\ {}^4P_1$	9.	3344.43	$3s\ {}^4P_1 - 3p\ {}^4D_1$
5.	3694.22	$3s\ {}^4P_3 - 3p\ {}^4P_3$	10.	3334.837	$3s\ {}^4P_3 - 3p\ {}^4D_4$
6.	3557.84	$3s\ {}^2P_1 - 3p\ {}^2S_1$			

C. J. BAKKER: THE ZEEMAN-EFFECT IN THE SPECTRUM OF IONIZED NEON (Ne II).



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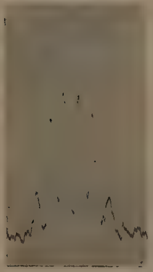

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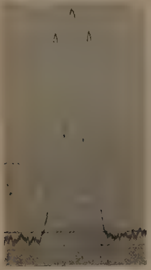

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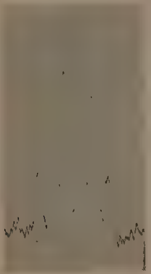

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Proceedings Royal Acad. Amsterdam. Vol. XXXII. 1929.

Physics. — *The existence in a mono-axial crystal of two different values for the magnetic rotation of polarisation in directions parallel with the axis and perpendicular to it.* By JEAN BECQUEREL. (Communicated by Prof. W. J. DE HAAS.)

(Communicated at the meeting of September 29, 1928).

Until now the magnetic rotation of the plane of polarisation by a mono-axial crystal in directions forming an acute angle with the axis, had not been investigated thoroughly. The rotation is usually covered by the double refraction as soon as the wave-normal deviates a little from the optical axis.

There are however crystals, containing rare earths that possess a great magnetic rotatory power. Among these tysonite $\{(\mathrm{La, Ce, Na + Pr})F_3\}$ has at the same time the greatest rotatory power and the weakest double refraction: $n_o = 1{,}6168$; $n_e = 1{,}6095 \ (\pm 0.0005)$ for the ray 5350 Å [1]). This mineral was therefore appropriate for the investigation of the magnetic rotatory power in directions oblique to the axis. We must remember here, that the negative magnetic rotatory power of tysonite (as of other crystals of rare earths) is of *paramagnetic origin*. This follows from the simple long-known fact [2]) that the rotation increases considerably as the temperature falls and is nearly inversely proportional to the absolute temperature T (at least as long as the temperature is not exceedingly low): the analogy with the law of CURIE is evident. Researches made at Leyden in collaboration with Prof. Dr. W. J. DE HAAS will soon be published at *temperatures of liquid helium* (from 4.2° K.—1.39° K.). The result of these experiments is, that at these temperatures *the magnetic rotatory power is a function of* $\frac{H}{T}$; *it is no longer proportional to the external field* H *but approaches a saturation value.*

This is the complete proof that the phenomenon is caused by a paramagnetic orientation. It is evident that on the paramagnetic rotation a diamagnetic one is superposed, but at very low temperatures the latter is (at least for tysonite) negligible compared with the paramagnetic rotation. Even at room temperature it seems to be still very weak.

We will describe here the experiments at room temperature.

---

[1]) Measurements of Mr. GAUBERT.

[2]) JEAN BECQUEREL, le Radium **5**, 16, 1908.
JEAN BECQUEREL et H. KAMERLINGH ONNES, Comm. Leiden N⁰. 103, le Radium **5**, 228, 1908.

I. *The apparatus.*

The measurements were made with the following apparatus.

A plate of tysonite (thickness $e = 1{,}866$ mm.), previously carefully ground perpendicular to the axis by Mr. WERLEIN, was put between the poles of a small WEISS electro-magnet. It was mounted in platinum at the extremity of a glass rod, the upper part of which was connected with the needle of a divided circle.

By trials we succeeded in fixing the plate so that the axis of the crystal remained horizontal, when the needle of the dial and with it the plate were turned round a vertical line. Then linearly polarised light (the electric vector vertical) is thrown on the plate [1]). When we let the transmitted light pass through an analysor crossed with the polarisor, the light must be extinct for any position of the plate.

Now the plate remains fixed in this way as well as the polarisor. For the measurement of the rotation I used a half-shadow-apparatus of Cornu; the image of the line of intersection falls on the widened slit of a spectroscope. When the analyser is turned, the line of separation between the two planes becomes oblique, but this does not matter for the observations.

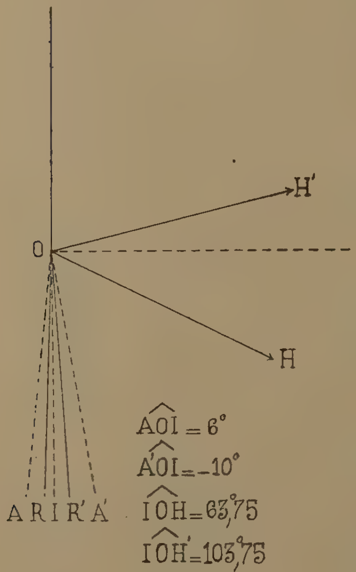

Fig. 1.

The light source was a mercury-arc-lamp. Though the rotatory power decreases with increasing wavelength it was preferable to use the green line, ($\lambda = 5460.7$) as this is more intense than the blue and violet lines.

The electro-magnet was mounted on a foot that could be rotated and supplied with a horizontal circular dial on which the direction of the magnetic field could be read.

The angles on both sides of the incident beam, within which the direction of the crystal axis varied, were 10° and 8° (fig. 1).

To the field different directions were given, which made angles with the incident light varying between 63°.75 and 103°.75 as has been indicated in the figure.

The changes in the direction of the electro-magnet from the transverse position with respect to the light beam thus took place as much in one sense as in the other.

---

[1]) It is unnecessary that the incident electric vibration is accurately vertical. It is required, that the optical axis of the plate remains perpendicular to the incident electric vibration, when the glass rod is turned.

II. *Adjustment of the crystal-axis parallel to the incident beam.*

The most simple method to adjust the axis parallel to the incident light is the realisation of the extinction between crossed nicols that form angles of 45° with the horizon. This method is not very accurate however because of the weak double refraction of the crystals. That is why we preferred the following method. The incident light is polarised under an angle of 45° with the horizon; the analysor is put directly behind the slit of the spectroscope and crossed with the polarisor. On the slit a Babinet compensator is fixid, orientated in such a way that the central band is perpendicular to the slit and about at the height of the middle of the slit. As is known, this combination gives a fan-shaped spectrum, when no double-refracting plate is placed in the way of the light. The middle band is a black one crossing the whole spectrum perpendicular to the spectral lines. The other bands are oblique in such a way that their mutual distances are smallest towards the short wavelengths.

When the light beam crosses the crystal plate and the axis is turned in the horizontal plane, the bands remain equally distinct, but they are displaced. Now we first fix the crystal plate with its axis as perpendicular as possible to the incident light, then we centre the point of intersection of the wires in the eyepiece on the central band. Then we turn the crystal without changing the position of the wires (keeping the axis of the crystal horizontal) first in one direction. We note the positions *a*, *b*, *c*, *d*... of the needle on the divided circle, for which the successive bands pass through the points of intersection of the wires. Then we bring the crystal back into its original position and turn it in the opposite direction. During this we note in the same way the positions *a′*, *b′*, *c′*, *d′*... of the needle.

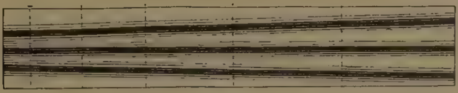

Fig. 2.

If the plate is cut exactly perpendicular to the axis the positions *a* and *a′*, *b* and *b′*, lie symmetrically i.e. the readings *a* and *a′*, *b* and *b′* give, when taken in pairs, as mean value the zero position in which the crystal axis is perpendicular to the incident light.

In reality the different mean values obtained in this way differ some tenths of a degree. Moreover they show no systematic change with the increase of the angle of incidence[1]). From this we may conclude, that *the plate may be regarded as accurately normal to the axis.* The mean deviation from the zero value from the observation of 5 to 6 bands in 2 or 3 series of measurements is not more than 0°.1. If in this way we know which division line of the dial corresponds to the „zero-position", we know for every orientation of the crystal the angle between the axis and the incident light which is at the same time the angle of incidence.

III. *Measurement of the difference in phase for oblique directions of incidence.*

With the aid of a compensator the phase difference can be measured between the two waves transmitted through the plate for every angle of incidence and for every wavelength.

After having adjusted the crystal in the zero-position we centre the intersection point of the wires on the point of intersection of the central band with that spectral line for which we want to carry out the measurements. Then we turn the plate over an angle i and measure the displacement of the band. The displacement divided by the distance of two successive bands is the phase difference. In this way the curve $\varphi_0 = f(i)$ may be constructed. For small angles of incidence this curve may be regarded as a parabola.

The knowledge of the phase difference as a function of the angle of incidence is required for the determination of the rotatory power in directions forming acute angles with the axis, as will be seen further now.

IV. *Magnetic rotation of the plane of polarisation in the direction of the axis. Verification of the cosine law.*

When the incident light is parallel to the axis we must find the law of VERDET:

$$\varrho = \varrho_A \, H \cos\theta \, ,$$

where θ is the angle between the ray and the field and ϱ and ϱ_A are the rotations in the direction in question and in that of the field respectively. This has been verified by turning the electro-magnet each time through 5°.

The rotations ϱ are plotted against the position of the electro-magnet as read on the divided circle. This curve gives with satisfactory accuracy (to 0°.1 at least) the position for which the rotation is zero i.e. for which the field is perpendicular to light beam. We derive from it the angle θ for every position of the magnet. A ventilator kept the crystal at room temperature. During the measurements the temperature was read several times. The measurements were reduced to 293° K. under the assumption that the rotation is proportional to $\frac{1}{T}$.

---

[1]) A statistical consideration of mean values of a and a' on one hand and of b and b', c and c' on the other hand, obtained from 10 series of measurements shows, that their deviations are negligible.

The following results are obtained:

θ	63°.63	68°.63	73°.63	78°.63	83°.63	88°.63	89°.63	93°.63	98°.63
Rotation measured	—12.71	—10.53	—8.08	—5.63	—3.13	—0.70	—0.15	+1.78	+4.26
„ calculated	—12.71	—10.42	—8.06	—5.61	—3.16	—0.69	—0.18	+1.80	+4.27

The first row gives the observed rotations reduced to 293° K.

The second row gives the rotations calculated with the cosine law, while the largest observed rotation has been assumed to be right.

We thus find:

$$\varrho_A H = -28{,}61.$$

For the field H, measured with a GRASSOT-fluxmeter we found 24830. Taking this value, we find for the constant of VERDET

$$V_A = \frac{\varrho_A}{e} = -6{,}175 \,.\, 10^{-3},$$

where the rotations have been given in degrees and the centimeter has been taken as unit of thickness. It is evident, that longitudinal measurements with pierced pole-pieces (the above measurements were made with massive pole-pieces) will give the same constant, but for inaccuracies in the determination of H.

V. *Magnetic rotation in directions oblique to the axis. Law of the phenomenon. Determination of the rotatory power perpendicular to the axis.*

In our experiments the crystal was only weakly double-refracting and moreover the angle between the incident ray and the axis (the plate was cut perpendicular to the axis) did not exceed 10°. In our discussion we might therefore treat the normals of the two refracted waves as coinciding and call their common direction the broken ray.

If the rotatory power of the crystal did not depend on the direction of the light, the influence of the field would always become zero when the broken ray was perpendicular to the field.

The following result shows that this is not the case. When the angle, formed by the field in either sense with the incident wave normal, is smaller than 4°, we always find an orientation of the crystal corresponding with an angle of incidence less than 8°, for which the influence of the field is zero. The experiments have taught, that to two directions of the field, forming together an angle of 5°, there belong two directions of orientation of the axis of the crystal for which the rotation is zero. The angle between these latter two directions is $10^1/_4$°.

Now we may easily calculate that this last angle would be much greater, if the influence of the field vanished for a perpendicular position of the broken ray with respect to the field.

In reality we have not one broken ray, but two broken rays, forming an angle of 5°. When we call the angles of refraction positive when they are acute with respect to the axis, we have

$$i_2 - r_2 - (i_1 - r_1) = 5^\circ.$$

As, further, the angle between the two positions of the axis is equal to $(i_2 - i_1)$ and the angle of incidence is so small, that we may write $i = nr$, this becomes:

$$i_2 - i_1 = \frac{n}{n-1}\, 5^\circ.$$

As the ordinary refractive index for tysonite is 1.6168 for 5350 Å, we may assume $n_0 = 1.616$ for the green mercury line 5460 Å. We then find

$$i_2 - i_1 = 13.1^\circ.$$

The difference of nearly 3° with the experimental result is much too large to be ascribed to possible errors, because the vanishing of the influence of the field or, what comes to the same, the *change in sign* of the effect is easily observable. No errors greater than $^1/_4$° are made in the determination of the position of the crystal. Moreover, as mentioned already, the experiment has been arranged in such a way, that we need neither the determination of the zero-position of the crystal, nor that of the position of the electro-magnet for which the field is perpendicular to the incident light, but only the observation of the change in sign of the rotation by a small rotation of the crystal.

The above proves indirectly, that the rotatory power must depend on the direction of the incident light. By reasons of symmetry we are led to the introduction of one rotatory power parallel to the axis and one rotatory power perpendicular to the axis, which together determine the rotatory power in an arbitrary direction.

The question arises, whether the phenomenon follows the law we obtain simply by generalizing the law of VERDET. For the idea is natural, that we have to take the components of the field in the directions of the axis and of the normal to the axis (in the plane through field and direction of the axis), and afterwards to project these two components on the direction of this broken ray.

In fig. 3 r and θ represent the angle of refraction and the angle between axis and field reckoned positive in the above mentioned way.

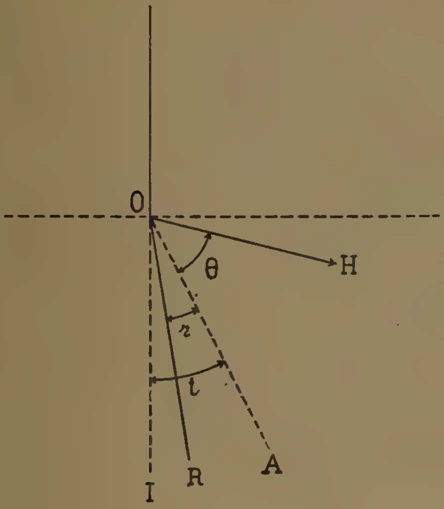

Fig. 3.

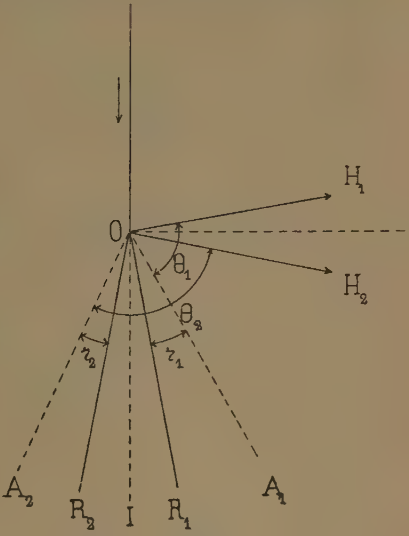

Fig. 4.

If V_A and V_N are the principal constants of VERDET, and if $\frac{e}{\cos r}$ is the traversed thickness of the plate, we must have

$$\varrho = V_A \frac{e}{\cos r} H \cos\theta \cos r + V_N \frac{e}{\cos r} H \sin\theta \sin r,$$

for which we may write:

$$\varrho = \varrho_A H \cos\theta + \varrho_N H \sin\theta \, tg\, r \, . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

If this law is true we find the value of ϱ_N from the observations of the zero-positions of the crystal for two directions of the field. The rotation is zero, when

$$tg\,\theta \, . \, tg\, r = - \frac{\varrho_A}{\varrho_N}.$$

As r is small and as θ differs little from $\frac{\pi}{2}$ we may replace $tg\, r$ by r and $tg\,\theta$ bu $\frac{1}{\alpha}$, where α is the complement of θ. This gives:

$$\frac{r}{\alpha} = - \frac{\varrho_A}{\varrho_N}.$$

We may also write with sufficient approximation $i = nr$; for two sets of values i_1, θ_1 and i_2, θ_2, for which the rotation is zero (fig. 4) we now find:

$$\frac{i_2}{\alpha_2} = \frac{i_1}{\alpha_1} = \frac{i_2 - i_1}{\alpha_2 - \alpha_1} = \frac{i_2 - i_1}{\theta_1 - \theta_2}.$$

If ψ is the angle between the direction of the field and the prolonged incident ray. we have:

$$\theta = \psi + i$$

so that:

$$\frac{i_2}{\alpha_2} = \frac{i_1}{\alpha_1} = \frac{i_2 - i_1}{-(i_2 - i_1) + (\psi_1 - \psi_2)}$$

and finally:

$$\frac{\varrho_A}{\varrho_N} = -\frac{r}{\alpha} = -\frac{1}{n} \cdot \frac{i}{\alpha} = \frac{1}{n} \cdot \frac{i_2 - i_1}{(i_2 - i_1) - (\psi_1 - \psi_2)}.$$

For $\psi_1 - \psi_2 = 5^\circ$ we have measured $i_2 - i_1 = 10.25^\circ$. With $n = 1.616$ this gives

$$\varrho_N = 0.828\, \varrho_A$$

with a possible error of $\pm 4^1/_2\,{}^0/_0$, as every position with rotation zero has been determined accurately to $^1/_4{}^\circ$ above or below the right value. Here we must remark that, ϱ_N and ϱ_A having the same sign, the rotatory power perpendicular to the axis has also the same sign (the so-called negative sign) as that parallel to the axis.

VI. *Experimental verification.*

In order to test the above-mentioned law we must see whether the rotations calculated with formula (1) agree with the observations.

In this formula ϱ is the rotation without the effect of the double-refraction and therefore not the measured rotation. Experimentally we determine with the half-shadow-apparatus *the rotation of the major axis for the elliptically polarised light by superposition of the rotation of the plane of polarisation and the double-refraction*. In order to compare the calculation with the experiment we must therefore calculate the rotation of this major axis. This can be done by means of the *representation on a sphere given by* POINCARÉ. A short exposition of this method will be useful.

For a given radiation and a given direction of propagation we consider all elliptical vibrations represented by all possible excentricities and orientations in the waveplane. Fig. 5 may represent one of these ellipses inscribed in a rectangle $ABCD$ with its sides parallel to the principal axis.

Further we introduce two axes of coordinates OX and OY. The angle between the major axis $O\xi$ of the ellipse and the positive direction OX (reckoned positive in the direction of a rotation from OX towards OY over an angle equal to or smaller than 180°) will be called $\frac{L}{2}$, so that $\frac{L}{2} \leqslant \pi$.

By $\frac{l}{2}$ we represent the angle between $O\xi$ and the diagonals of the ellipse. Thus $\frac{l}{2} \leqslant \frac{\pi}{4}$.

We agree to plot this angle starting from $O\xi$ in positive direction when the ellipse is left-handed (as in the case in fig. 5) and in negative direction. when the ellipse is right-handed.

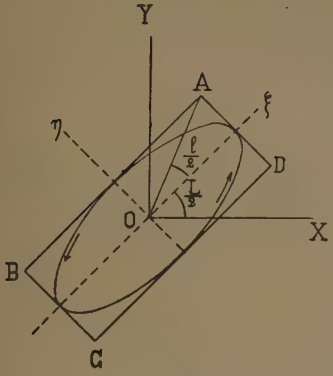

Fig. 5.

In this way elliptically polarised light is quite determined but for its intensity.

Further we consider (fig. 6) a sphere with radius one. We choose two poles P_g, P_d and a fundamental meridional plane $P_g X P_d$. We let a point M on this sphere determine the orientation and the form of an ellipse and the direction in which it is described in the following way.

As longitude of M we take the angle L, so that: $L = XCm$, reckoned from 0 to 2π from X in positive direction.

As latitude of M we take the angle l, so that $l = mM$, reckoned from 0 to $\frac{\pi}{2}$ from the equation along the meridian $P_d m P_g$.

Further we reckon the ellipse left-handed, if M lies on the hemi-sphere, of the pole P_g, which will be called the northern hemisphere and right-handed, if M lies on the southern hemisphere i.e. on the side of the pole P_d.

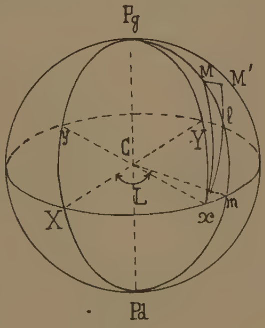

Fig. 6.

This being fixed, the following is evident:

1. Every point of the equator represents linearly polarised light. Two diametrically opposite points of the equator represent two light-beams polarised perpendicular to each other.

In general two points lying at the extremities of an arbitrary diameter represent two elliptically polarised rays, for which the ellipses have the same excentricity, while their axes are crossed and they are described in opposite senses.

2. The poles P_g, P_d represent resp. left and right circular polarised light.

3. Points on the same parallel circle belong to ellipses with the same excentricity and described in the same sense, but differently orientated.

Rotation of the plane of polarisation.

After the above it is clear how the rotation of the plane of polarisation is represented.

If elliptically polarised light falls on a non-double-refracting plate with rotatory power, the elliptic vibration M will not be deformed, but only notated. This rotation over an angle ϱ is represented in the figure by a rotation of the point M through an angle 2ϱ about the line through the poles $P_g P_d$.

Double-refraction.

Elliptically polarised light may now fall on a double-refracting plate, that does not possess rotatory power. The two rectilinear vibrations that are transmitted unaltered by the plate are represented by two diametrically opposite points x and y of the equator.

x may represent the slower transmitted vibration; by φ_0 we represent the *positive* retardation expressed in the number of vibrations, which the component x of an arbitrary vibration M suffers, compared with the component y.

It is evident that this influence of the crystal plate is represented in the figure by a rotation in positive sense i.e. in the direction of the hands of a clock about the axis $x \rightarrow y$ *through an angle* $2\pi\varphi_0$. *In fig.* 6 M *is displaced in this manner towards* M'.

Rotation of the plane of polarisation + double-refraction.

Finally the double-refracting plate may also possess rotatory power.

Evidently the influence of this plate may be represented graphically by addition of the rotations $2\pi\varphi_0$ about xy and 2ϱ about $P_g P_d$ i.e. by rotating M through an angle

$$2\pi\varphi = \sqrt{4\pi^2\varphi_0^2 + 4\varrho^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

about the oblique axis $N_d N_g$.

This axis is the diagonal of a rectangle with the sides $2\pi\varphi_0$ and 2ϱ along xy and $P_g P_d$ (fig. 7). The points N_d and N_g correspond to the ellipses of AIRY, which are transmitted unaltered.

This graphical representation of POINCARÉ we are now going to apply in order to derive a formula by which we can test the generalised law of VERDET with our observations.

For all positions of the crystal plate the incident vibration is perpendicular to the axis of the plate and thus forms the ordinary ray which remains rectilinear in the absence of a magnetic field. Therefore we may represent it by the point x (fig. 7).

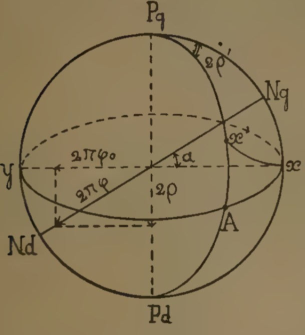

Fig. 7.

Under the influence of a given field and for a position of the optical axis deviating from its zero-position the point x turns about an oblique axis $N_d\,N_g$ and comes to x'.

The quantity, measured with the half-shadow-apparatus, is the rotation of the major axis of the ellipse. This rotation will be called ϱ'; it is half the angle between the meridional planes $P_g\,x\,P_d$ and $P_g\,x'\,P_d$.

We draw the large circle arc $x'N_g$ and consider the spherical triangle $P_g\,x'\,N_g$. In it:

1. The side $x'\,N_g$ is equal to the arc $N_g\,x$. Calling this length a, we find from the construction of the axis $N_g\,N_d$:

$$tg\,a = \frac{\varrho}{\pi\,\varphi_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

2. The side $P_g\,N_g$ is equal to $\frac{\pi}{2} - a$.

3. The angle N_g is $\pi - 2\,\pi\,\varphi$.

The formulae of spherical trigonometry now give the relation:

$$cot.\,P_g \equiv cot.\,2\,\varrho' = \frac{cos^2\,a + cos\,2\,\pi\,\varphi\,.\,sin^2\,a}{sin\,2\,\pi\,\varphi\,.\,sin\,a} \quad . \quad . \quad . \qquad (4)$$

This formula gives indirectly through the angles a and $2\,\pi\,\varphi$ the relation between the combined effect and the double refraction and the simple effect of the pure magnetic rotation.

Let us suppose that formula (1) represents the law of the phenomenon. We have derived already ϱ_N from it (§ V). As we know $\varrho_A H$ and $\varrho_N H$ we can now calculate ϱ for any orientation of the field and any orientation of the crystal axis. As, on the other hand, φ_0 is known from the curve $\varphi_0 = f(i)$ (§ III) we can calculate $2\,\pi\,\varphi$ and a with the formulae (2) and (3). Finally formula (4) gives the rotation ϱ' of the major axis of the ellipse.

In this way the full lines in fig. 8 have been calculated. These are therefore theoretical curves, equivalent to the law represented by formula (1). They give the rotation of the major axis of the ellipse of the incident light as a function of the angle of incidence for the different positions that were given to the magnet during the experiments. The angles indicated in the fig. (68.75° — 103.75°) represent the angles formed by the field with the direction of the prolonged incident ray (see fig. 1). The dotted curves are those we should have obtained, if the rotatory power did not depend on the direction and had been equal to that measured along the axis[1]). The marked points give the measurements.

Though the deviations between the two families of curves are not very large and the observation errors sometimes may be of the same order of magnitude, it is still evident, that the full curves agree best with the measurements. We must especially point to the fact, that the dotted curve VI must be rejected, as it gives a rotation zero for $i = -9.8^\circ$, while the observations make it absolutely certain that the rotation changes its sign between -7° and -8°. This fact alone shows already that the rotatory power cannot be independent from the direction.

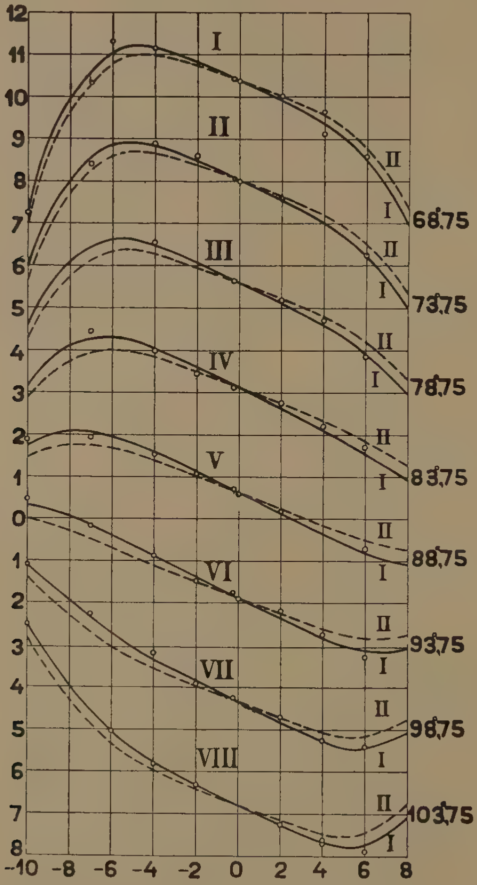

Fig. 8.

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[1]) In the figure those rotations have been plotted as positive ordinates, which have the same sense that would be observed when both the crystal axis and the field had the direction of the incident light-beam.

Already beforehand we can tell, that the enormous rotations observed at very low temperatures form an excellent confirmation of the above mentioned law. Or more accurately: the rotations being no longer proportional to the intensities of the field, the observations gave the confirmation of the law in more general form, while for smaller values of $\frac{H}{T}$ formula (1) is again found.

Finally I wish to express my sincere thanks to Mr. LOUIS MATOUT sub-director of the physical laboratory of the museum for his valuable assistance in the preparation of the apparatus and in the performance of the measurements.

Physics. — *The law of magnetisation of solid crystals. Resolution of the* FARADAY-*effect into two effects of different origin. Diamagnetic and paramagnetic rotation of the plane of polarisation.* By JEAN BECQUEREL and W. J. DE HAAS. (Communication N⁰. 193*a* from the Physical Laboratory at Leiden.)

(Communicated at the meeting of September 29, 1928).

I. *Introduction.*

In a summary of earlier researches, twenty years ago, one of us [1]) drew attention to the following fact: *the rotatory power of some minerals that contain rare earths* (erbium, neodymium, praeseodymium) *increases considerably when the temperature falls and is inversely proportional to the absolute temperature.* Such a remarkable correspondence with the law of CURIE led the first author to prove the existence of a rotatory power that is intimately connected with paramagnetism. In paramagnetic bodies this rotatory power is superposed on the diamagnetic rotatory power, which is connected with the ZEEMAN-effect and is just as general as this.

We now give the decisive proof of the existence of the paramagnetic rotation of the plane of polarisation. But before describing our experiments we will give a historical review of the problem. Long ago we find the idea of a connexion between the FARADAY-effect and the magnetic properties of a body. Defended by some physicists, disputed by others, this hypothesis has given rise to may discussions.

Four years after the discovery of FARADAY EDMOND BECQUEREL [2]) showed, that the salts of iron in aqueous solution considerably diminish the magnetic rotatory power of the liquid. This induced VERDET [3]) to ascribe to the salts of iron a rotatory power opposite to that found in all experiments of FARADAY. VERDET distinguished these two directions as positive [4]) (water, glass, etc.) and negative.

An obvious hypothesis is, that the negative sign given by iron salts is caused by their magnetic properties, that as a rule diamagnetic substances give a positive rotation and paramagnetic bodies a negative one. Titanium tetrachloride, although diamagnetic, gives a negative rotatory power. In Verdet's opinion this fact proved the independence of the sign of rotation upon the magnetic properties. Henri Becquerel [1]) studied the magnetic substances. He found, that "the magnetic rotation of the bodies is connected with their refractive index and with another function that varies with their specific magnetism". For the first time he showed the connexion between the rotatory power and the magnetic properties of matter.

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[1]) JEAN BECQUEREL, le Radium **5**, 16, 17, 1908; Rapports présentés au premier congrès intern. du froid **2**, 43, 44, 1908.

JEAN BECQUEREL et H. KAMERLINGH ONNES, Comm. Leiden n⁰. 103; le Radium **5**, 238, 1908.

[2]) EDMOND BECQUEREL, Ann. de Chimie et de Physique, 3e série, **28**, 334, 1850.

[3]) VERDET, Ann. de Ch. et de Phys. 3e série, **52**, 144, 1858.

[4]) The rotation is called positive, when to the observer receiving the light that is propagated in the direction of the lines of force, the plane of polarisation is rotated anti-clockwise.

Unfortunately at that time (1876) the knowledge of the origin of magnetic phenomena was practically nil, so that the causes of the Faraday-effect could not be found out. Henri Becquerel ascribed the negative rotation to the production of an internal magnetic field with sign opposite to that of the external field, an hypothesis which has been taken up again by several physicists. Though the idea was plausible, our investigations lead the problem in another direction in connexion with the actual theories of magnetism.

We must now remember an important phenomenon discovered in 1884 by Kundt [2]) : Ferromagnetic metals in leaves so thin as to let through enough light (some thousandths of a millimeter) possess an enormous magnetic rotatory power. The rotation is not proportional to the external field ; it asymptotically approaches a limit. According to Du Bois [3]) the rotatory power is proportional to the *magnetisation* and is *positive*.

One of the principal reasons of Drude for advancing his theory called : "the hypothesis of the molecular currents" [4]) was the explanation of the Kundt-effect. Drude assumes in paramagnetic bodies the existence of special currents which are partially or wholly directed in the magnetic field. In diamagnetic bodies these currents would not previously exist, but they would only be induced by the external field. In the most simple case this theory gives a rotatory power proportional to the magnetisation and leads to variations of the rotatory power of opposite sign at the two sides of an absorption band, both for diamagnetic and for paramagnetic bodies.

In his "Lehrbuch der Optik" Drude gives yet a second theory, which he calls the "hypothesis of the Hall-effect". This theory is the same as that given before by W. Voigt [5]) : the magnetic rotatory power is a consequence of the Zeeman-effect and of the dispersion. At both sides of an absorption band the variations in the rotatory power must have the same sign, in contradiction with the other theory.

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[1]) Henri Becquerel, Ann. de Ch. et de Phys. 5e série **12**, 42, 1877. We remember, that in 1897 (C. R. **125**, 679) H. Becquerel gave a theoretical expression for the magnetic rotation. This expression is identical with that which was afterwards derived from the Larmor precession; it concerns the diamagnetic rotation.

[2]) A. Kundt, Wied. Ann, **23**, 228, 1884; **24**, 191, 1886.

[3]) H. du Bois, Wied. Ann. **31**, 941, 1887.

[4]) Drude, Lehrbuch d. Optik, 406, 1906.

[5]) W. Voigt, Wied. Ann. **67**, 345, 1899; Ann. d. Phys. **6**, 784, 1901; **8**, 872, 1902.

W. Voigt does not seek the origin of the Faraday-effect in the magnetisation and he disputes the theory of the "molecular currents". He expresses the opinion that the external field can give rise to internal forces [1]) which for magnetic bodies may be nearly proportional to the magnetisation, so that for thin leaves of ferromagnetic metals a direct influence of the magnetisation on the magnetic rotatory power seems to exist. He comes back to the idea of a field of sign opposite to that of the external field. As to the sign of the Kundt-effect, which is positive notwithstanding the reversal of the field, this would be explained by the absorption being due to "free electrons".

At the time of the publication of the work of W. Voigt (1908) the greater part of the physicists kept to the "hypothesis of the Hall-effect", at least for non-conducting bodies. The theory found its origin in the experiments of Macaluso and Corbino and of several physicists on the rotatory power of vapours in the neighbourhood of lines that show the Zeeman-effect. One of us extended these investigations to solid bodies by experiments on the magnetic rotatory power of crystals of rare earths in the neighbourhood of those absorption bands, for which the absorption of oppositely circular polarised rays had the same value. Even a *quantitative* verification of the theory was given [2]).

On the other hand an important fact was observed in the course of the investigations of crystals of the rare earths. For many bands the opposite circular rays were unequally absorbed under the influence of a magnetic field. A dissymmetry existed for the two circular components. This new phenomenon was directly considered in connexion with paramagnetism [3]).

Here follows, what was written in 1906:

"In my opinion, we have here to do with an intrinsic manifestation of "the molecular magnetism. The projection of the motion of each electron on "a plane perpendicular to the axis may be resolved into two opposite circular "vibrations. When we suppose, that the paths of the electrons or certain "groups of electrons can be orientated under the influence of the external "field and that the sum of the circular motions in one direction becomes "perceptibly different from the sum of the oppositely directed motions, one "component becomes stronger with respect to the other and a dissymmetry "in the intensities is observed.

"......On the other hand the electrons together will be equivalent to a "magnet directed along the lines of force. So the crystals of xenotime are "magnetic and a cube is orientated, so that the axis becomes parallel to "the field.

"By means of a quarter-wavelength plate combined with a Babinet "compensator it is proved, that the circular double refraction i.e. *the*

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[1]) W. Voigt, Magneto- und Elektrooptik, 21. 1908.

[2]) Jean Becquerel, le Radium 5, 15, 1908; W. Voigt, Magneto- und Elektro-optik § 133, 232.

[3]) Jean Becquerel, C. R. de l'Ac. des Sc. **143** (24 déc. 1906).

"*magnetic rotation of the plane of polarisation, has opposite signs at the* "*two sides of the band......*

"The rotatory power varies rapidly in the neighbourhood of the band "notwithstanding its small intensity. The facts may easily be explained "by noticing that, because of the considerable inequality between the two "components, the anormal dispersion for one circular vibration is much "greater than for the other.

"The question arises, whether the anomalies shown by magnetic bodies "and the great dispersion of the rotation for some of them may not be "connected with a phenomenon of the same nature. The deformations of "the linear vibrations, especially after their passage through the iron leaves, "may be caused by a similar effect."

Thus the different dissymetries in the intensities and the effect of the magnetic rotation of the plane of polarisation have been ascribed long since to a paramagnetic orientation 1). The theory of VOIGT treats the magnetic rotation, but it does not explain the paramagnetic rotation or rather, for this phenomenon the theory must be completed by introduction of the effect of the orientation, which causes an inequality in the absorption of oppositely directed circular vibrations. This was said shortly in one of the sentences of the above quoted passage. Recently R. LADENBURG 2) did the same. Without knowing the above cited paper, he proceeded from the same ideas and expressed them in mathematical form. R. LADENBURG also did not go further as he too gave a theory of the dispersion of the paramagnetic rotation of the plane of polarisation.

The lower the temperature, the better do the intensities show the dissymetry of paramagnetic origin 3). We observed that at a temperature of 4.2° K. and in a field that need not be strong (10000 Gauss) some bands absorb circular vibrations of only one direction 4).

Apart from local disturbances caused by absorption bands in the visible spectrum, the great rotatory power of crystals that contain rare earths and its increase with fall of temperature must be due to strong absorption bands in the ultra violet.

In the earlier experiments, which were all made at room temperature or at higher temperatures, only relatively low values were found for the

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1) Of the more recent papers on paramagnetic rotation must be mentioned those of ELIAS on the rare earths (Ann. d. Phys., **35**, 298, 1911); those of ROBERTS, SMITH and RICHARDSON on salts of iron and cobalt in solution (Phil. Mag. **44**, 917, 1922; **49**, 397, 1925); and those of DORTMANN on the dispersion of the magnetic rotation of liquid oxygen and on the solutions of salts of rare earths (Zeitschr. f. Phys. **17**, 93, 1923).

2) R. LADENBURG, Zeitschr. f. Phys. **34**, 898, 1925; **46**, 168, 1927. The discussion of the work of LADENBURG must be postponed until our next paper. There we shall show that our experiments agree within one thousandth with the dispersion law of LADENBURG.

3) JEAN BECQUEREL, le Radium **5**, 9, 1908; JEAN BECQUEREL and H. KAMERLINGH ONNES, Comm. Leiden n⁰. 103 (§ 10), 1908; JEAN BECQUEREL, le Radium, **6**, 330, 1909.

4) JEAN BECQUEREL, H. KAMERLINGH ONNES and W. J. DE HAAS, Comm. Leiden n⁰. 177, 1925.

paramagnetic rotatory power. According to the circumstances it was the paramagnetic or the diamagnetic effect that predominated. It is evident, that at that time many physicists did not recognize the connexion between the direction of the rotatory power and the magnetic properties. Therefore it is interesting, that HENRI BECQUEREL felt convinced of the existence of such a connexion, because he had observed that a substance with a negative rotatory power (e.g. $TiCl_4$) always contained a paramagnetic component.

It was also this rule, which induced one of us to make use of low temperatures for the separation of the paramagnetic from the diamagnetic effects in magneto-optical phenomena [1]). We must remark, that the paramagnetic rotation need not be negative [2]). In transparent substances however this is the sign which has been found until now at the side of the long wavelengths compared with those of the active bands for which the effect predominates.

II. *The experiments. The cryostat.*

We shall omit a description of the spectroscopic arrangement. This is the same as that used in the physical laboratory of Prof. BECQUEREL since 1906, afterwards used also at Leiden in 1908 and 1924. We only mention again, that we used a plane ROWLAND grating with 568 lines per mm., 8 cm. wide and provided with auto-collimation with a lens of 1.3 m. focal length. The spectra observed or photographed were of the first or second order. The source of light was an arc-lamp.

The cryostat consists of three vacuum glasses. In the innermost one the liquid helium boils, in the second which surrounds the first, liquid hydrogen boils and in the glass surrounding the first two boils liquid nitrogen. The glasses were blown with great skill. The inner tube of the helium-glass has a diameter of 5 mm., the outer tube of the nitrogen-glass one of 15 mm. The light must pass through twelve glass walls and five layers of liquid. The pressure of the helium which boils in the inner glass is measured by means of a closed mercury manometer. During an experiment the pressure is kept accurately constant by means of a regulating cock.

In the cryostat cap a metal rod can both turn round its longitudinal axis and be moved up and down. To this metal rod, in the cryostat, a glass rod has been glued at the end of which the holder for crystals is glued. By vertical displacement each crystal may be brought into the beam of light and if necessary the crystal axis may be turned in a horizontal plane.

III. *Object of the investigation. Measuring method.*

The object of the investigations was the determination, for some wavelengths and for some very low temperatures, of the variation of the magnetic rotatory power as a function of the intensity of the field. Among the monoaxial crystals one seems especially suited for this research viz. *tysonite* ((La, Ce, Nd + Pr) F_3) because of the following reasons :

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[1]) JEAN BECQUEREL, le Radium, **5**, 6, 1908.

[2]) See LADENBURG, Zeitschr. f. Phys. **34**, 903, note; **46**, 172 and 176.

1⁰. Of the crystals investigated until now tysonite has the greatest magnetic rotatory power.

2⁰. The crystal is beautifully transparent and can therefore be used in thicker plates than other crystals. With a plate of 1.866 mm., which we possess and notwithstanding the twelve glass walls of the cryostat the spectrum is of good intensity.

3⁰. The absorption bands in the visible spectrum are nearly all combined into groups and for the greater part are little active except the band $\lambda = 5776$. Moreover they are separated by large intervals in which their influence can be neglected. When the wavelength is chosen within these intervals, only the principal phenomenon is observed, separated from all local disturbances. As the earlier investigations, mentioned in § I, had shown that the magnetic rotatory power must be of paramagnetic origin, we might expect to find at sufficiently low temperatures a deviation from the law of proportionality to the field strength, which law had always been found since FARADAY. It was even to be expected, that the rotation would be a function of $\frac{H}{T}$. We need not point out the importance of the determination of this function for the theory of magnetism.

For the study of this phenomenon a very accurate measurement is of course required, but before all we must choose a very quick method, if necessary somewhat sacrificing the accuracy.

Now at very low temperatures the magnetic rotatory power of tysonite is enormous, so that a determination of the rotations between 1500° and more thans 5000° to an accuracy of 1°, is not only unnecessary but of imaginary advantage, as the determination of the field with an accuracy of $^1/_{100}$° is already difficult.

The measurements must be made quickly in an uninterrupted series under conditions as fixed as possible; otherwise they are not well comparable after reduction to one and the same temperature. We have chosen the most simple method viz. that of the canaliculated spectrum.

The light of an arc-lamp is sent along the lines of force through the poles of an electro-magnet, which are pierced with holes of 1 mm. diameter. This beam is sufficiently parallel. The crystal plate which may be regarded as cut perfectly normal to the axis has been fixed with the greatest care with the aid of a BABINET compensator ¹) in such a way, that the axis is parallel to the incident light. When the compensator and analysor, which were used for the adjustment, are taken away, the incident light is so

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¹) This method has been described in the former communication of the Phys. Lab. Leiden N⁰. 191c II § 11. From measurements of the phase differences between the transmitted vibrations with oblique direction of incidence we conclude statistically that the position of the plate is sufficiently perpendicular to the axis.

polarised that the electric vector is vertical. We then put before the slit of the spectroscope a rhombohedrar of iceland spar which forms a double-refracting analysor. In this way we obtain two spectra in juxtaposition, and when there is no field the spectrum corresponding with the horizontal vibrations is extinct [1]).

The light of an iron arc-lamp, standing on one side, is reflected by a mirror and can be thrown on the slit of the spectroscope whenever we want to superpose the iron spectrum on that of the crystal in order to determine the wavelengths.

As soon as the current of the electro-magnet is switched on the magnetic rotation is observed and as the field increases we see that in the two adjacent spectra numerous black lines are displaced from the violet towards the red.

We now choose either from the iron spectrum, or from the absorption spectrum [2]) of the crystal the radiation for which we are going to make the measurements and we look at the passage of the black lines through the chosen spectral line. In this way we find the rotations $n\pi$ in the spectrum of the horizontal vibrations and $\left(n\pi + \frac{\pi}{2}\right)$ in the spectrum of the vertical vibrations.

At each passage we note the intensity of the current, which gives the intensity of the field, the curve that gives H as a function of the current having been plotted beforehand.

For this determination of the field as a function of the current we made use of the deviation of the components of the line 5221 of xenotine (at the temperature of liquid air). This line is fine and very sensitive, for it gives a deviation 8½ times that of the normal ZEEMAN-effect [3]).

The individual errors in the measurements can be of the order of 5 $^0/_{00}$ in a field of 30000 Gauss, and they are the greater the weaker the field. These errors may be corrected to a large extent by the form of the curve.

We have preferred this method because it gives the field *between the pole-pieces,* i. e. just at the place where we must know it.

The maximum field that was used (current of 150 Ampère, distance between the pole-pieces 16 mm.) was found to be 26.73 kilogauss.

The measurements were made at the following temperatures, and for the accompanying wavelengths.

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[1]) At very low temperatures the extinction is never total; for the residual magnetism of the pole-pieces is sufficient to give a rotation of several degrees.

[2]) We chose an isolated fine line, which is inactive or sufficiently so to cause no appreciable disturbance. We must still mention that the black line almost wholly covers the spectral line in one spectrum, but that this line remains visible in the other spectrum, which then has its maximum intensity. This makes the observations possible.

[3]) It is an acknowledged fact, that the deviation is proportional to the field. For the absolute measurements the calibration was made at Zürich in 1909. The deviation was determined on a cliché in a field, the intensity of which had been measured by Prof. WEISS (7.71 Å for 349000 G).

$$T = 4^\circ{,}21 \left\{ \begin{array}{l} \lambda = 4258{,}9 \text{ (line of tysonite)} \\ \lambda = 5328{,}5 \text{ (middle of an iron-doublet)} \\ \lambda = 6249{,}5 \text{ (line of tysonite)} \end{array} \right\} \begin{array}{c} \text{thickness of the} \\ \text{plate} \\ e = 1.866 \text{ mm.} \end{array}$$

$$T = 1^\circ{,}71^4 \left\{ \begin{array}{l} \lambda = 4258{,}9 \\ \lambda = 5328{,}5 \end{array} \right\} \text{ with two plates for which: } \left\{ \begin{array}{l} e_1 = 1{,}866 \text{ mm.} \\ e_2 = 0{,}675 \text{ mm.} \end{array} \right.$$

$$\left. \begin{array}{l} T = 1^\circ{,}41^2 \\ \text{and } 1^\circ{,}39^4 \end{array} \right\} \lambda = 5328{,}5 \quad \text{thickness of plate} \quad e = 1{,}866 \text{ mm.}$$

The given temperatures below 2° are a little incertain. We shall see further on why the above temperatures have been assumed.

The measured negative rotations are corrected for the positive rotation caused by the cryostat, which may not be neglected (5°, for 5890, 12.5° for 4000 Å).

IV. *Approach of the saturation. Law of the paramagnetic rotation as a function of* $\frac{H}{T}$. *The magneton.*

First we have plotted the curves of the rotations as a function of the field.

At 4.21° it is already evident, that *the rotation is no longer proportional to the field* 1). At temperatures of 1.7° and of 1.4° the deviation from proportionality is considerable.

We shall begin with the discussion of the results at 1.7°, which we found for two lines and with two plates of different thickness.

We plotted the curves $\varrho = f(H)$ in such a way that they represented the experimental results as truly as possible and without proconceived opinion i. e. without making use of any theoretical law. For all these different curves we have established that their ordinates bear a fixed ratio to each other viz. that the rotations found for *the same wavelength with two different plates are proportional to the thickness of these plates.*

Let e.g. *a* and *b* the experimental curves for the wavelengths 5328.5 and 4258.9 for the plate with $e = 1.866$ mm. We take all measurements for the violet line and their ratio to the ordinates of the curve *a* for the same field intensities. Then we take the observations for the green ray and the ratio's between the points of the curve *b* and the measured values for the green line. The mean of all these ratio's gives with very good accuracy the ratio between the rotations for the violet and for the green, which ratio is independent of the field (of the 32 values obtained 16 differ less than

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1) This deviation from the proportionality which is not large at 4.2° escaped our first observations (Comm. Leiden n⁰. 177) because we had confined ourselves to 3 determinations and the 3 values of the field intensity measured separately were not known with the same accuracy as those which are derived from numerous measurements and thus permit us to lot the field-current-curve.

2 $^0/_{00}$ from the common mean and the two largest deviations are only +7 $^0/_{00}$ and —5 $^0/_{00}$).

For the two plates used, the ratio of the rotations for the same wavelength proved to be equal within $^1/_{1000}$ the ratio of their thicknesses as measured with the comparator.

Thus the first result deduced from the experiments is that *the law of the variation of the magnetic rotatory power as a function of the field is independent of the wavelength*. The problem now is to find this law. After having measured, as has been said, the ratio's of the rotations for the two plates and for the two lines used we reduced all measurement to one curve C_1 which represents all measurements for the temperature considered (1.7°) and can be plotted in a very sure way.

Until now the only investigations that showed an approach to the saturation, were those of WOLTJER and KAMERLINGH ONNES [1]) with gadolinium sulphate. As these authors concluded from their investigations, that the law of magnetisation was that of LANGEVIN, we first tried to identify the curve C with that of LANGEVIN. We found however systematic deviations, which though not large, still exceeded the possible errors. Moreover it is natural, that the law is different from that of LANGEVIN, as the conditions are quite different from those for which he made his theory. We must keep in mind that the investigations of WOLTJER and KAMERLINGH ONNES were made with crystalline powder and not with an orientated crystal.

For the magnetisation in one of the principal directions of a crystal LENZ [2]) and afterwards EHRENFEST [3]) deduced in a theoretical way a more complete theory, in which the function in question contains the tangens hyperbolicus. We have tried this theory and this time with success. The curve C is represented as well as might be expected by the formula :

$$y = A \, tgh \, C H.$$

The value of C that gives the best agreement between the theoretical and experimental curves is :

$$C = 3.923.10^{-5}.$$

With this value of C the deviations of the theoretical curve from the experimental one are of the order of the width of a pencil-line on a plot of 80 × 80 cm. It is evident that the primary cause of the magnetic rotation is a magnetisation effect and we see that this relation is expressed by a simple law [4]).

The tangens at the origin coïncides with the curve over a considerable length ; this is the law of CURIE.

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[1]) WOLTJER and KAMERLINGH ONNES, Comm. Leiden n⁰. 167.

[2]) W. LENZ, Phys. Zeitschr. **21**, 613, 1920.

[3]) P. EHRENFEST, Comm. Leiden Suppl. n⁰. 44*b*.

[4]) At first view it seems surprising to find a simple law for a crystal containing three paramagnetic ions, but in a following communication we shall show, that the paramagnetic orientation is due to only one of these three ions.

There is no reason for introducing a molecular field worth considering. Nor is it necessary to take into account a demagnetising field, as the rotation is proportional to the thickness of the plate.

Assuming that the rotation is proportional to the magnetisation effect to which it is due (which seems to be true, though it has not been proved [1])), we must identity CH with the variable a of LANGEVIN ; just as in the theories of LENZ and of EHRENFEST. We then have :

$$C = \frac{\Sigma_\infty}{RT},$$

where R is the gas-constant and Σ_∞ the saturation-magnetisation reduced to a gram-molecule and expressed in the magnetic moment of the unit of magnetism the so-called magneton μ, which determines the phenomenon. So we can find Σ_∞, when the temperature is known.

For these experiments the pressure of the helium was reduced to 9 mm.

The temperature of helium boiling under a pressure of 9 mm. lies between 1.66° and 1.76° K. The temperature cannot be given with certainty, as the temperature-scale of the gasthermometer has not yet been fixed [2]).

With 1,66° we find $\Sigma_\infty = 0{,}968\ \mu_{Bohr} = \mu_B$
„ 1,76° „ „ $\Sigma_\infty = 1{,}026\ \mu_{Bohr}$.

Perhaps it is merely fortuitous, that the value of the BOHR magneton lies just between the values of Σ_∞ that are found with the two estimations of the temperature. But it is more probable that Σ_∞ is exactly the magneton. We must moreover keep in mind that for this orientated crystal we must consider the quantisation of the paths with respect to the common direction of the axis and of the field.

If we suppose it is established that $\Sigma_\infty = \mu_B$, then it is the temperature that is determined by our experiments. It is then 1.714°, except for the errors in the determination of the absolute intensities of the field and in the value of the magneton.

If it were possible to proceed with the measurements at 4.21° in the same way as we have just done, it would be possible to identify the experimental rotation curve at the known temperature of liquid helium under normal pressure with the tanh-line and no uncertainty would remain in the value of Σ_∞. At 4.21° however the magnetic moment is too small and the curvature too weak to identify the curve with sufficient certainty. Only the following is sure. If we plot curves of ϱ not as a function of H but as a function of $\frac{H}{T}$, then the curves of the measurements at 4.21° and those which we obtain by taking for the temperature of the above described experiments 1.714° have ordinates that bear in a remarkable way a fixed ratio to each other.

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[1]) At all events the proportionality has been proved for high temperature, the rotation and the magnetisation being then both proportional with the field.

[2]) Investigations on this subject are proceeding at Leiden.

Thus the law of the hyperbolic tangent represents not only the results for helium under a pressure of 9 mm., but also (but for a factor) the experimental results at 4.21° for the three lines used.

We might also assume 1.66° of 1.76° for the temperature of the reduced helium without appreciably disturbing the proportionality between the ordinates of the curves. The values of $\frac{H}{4.21}$ remain too small to deviate the tang-hyp. curve much from its tangent at the origin.

Finally the law of the hyperbolic tangent has been confirmed by two other series of measurements which we made after having reduced the pressure with two coupled Siemens pumps. If we start from the hypothesis, that the carrier of the magnetic moment has a magnetic moment equal to the magneton of BOHR, we find for the temperatures of the two series 1.41° and 1.39°. By application of the vapour tension formula of VERSCHAFFELT (pressure of the order of 2.8 mm.) we find a temperature of about 1.4°.

Fig. 1 represents the hyperbolic tangent obtained by reducing all measurements with the two plates for the different temperatures and for the different wavelengths to one curve with the aid of the previously determined ratios between the ordinates of each curve and those of one definite curve. The full curve is the hyperbolic tangent, calculated under the assumption of the BOHR magneton and the temperatures derived from it (see above) : 4.21°, 1.71°, 1.41°, 1.39°. Two scales of abscissae are given, the scale in $\frac{H}{T}$ and the scale for the variables a, where

$$a = \frac{\mu_B H}{RT}.$$

The ordinates are the rotations expressed in the saturation rotation viz. $\frac{\varrho}{\varrho_\infty}$. The last point corresponds with 85.7 % of the saturation.

The last points, obtained at the very lowest temperatures, are the result of measurements made with special care. At the temperature of 1.7° some uncertaintity existed in the determination of the strongest fields as may be seen in the figure (between the values 14300 and 15300 of $\frac{H}{T}$). The cause lies either in the fatigue of the observers towards the end of the series of measurements or in the fact that the method of the canaliculated spectrum becomes less sensitive the closer the black lines are together. The same error in the position of a black line gives then of course an increasing error in the magnitude of the rotation derived from it [1]). Perhaps also variations of the temperature play a role.

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[1]) In weak fields also the sensitiveness decreases but for another reason: the black lines become too wide. The increase in sensitivity by their large displacement for a small change in the field does not compensate for the decrease of the sensitivity by the difficulty in determining the middle of the lines.

We have therefore repeated the experiments and lowered the temperature still more in order to enter a region where the curve shows a strong curvature. We concentrated our forces principally upon the determination of the last points (means of several observations), so that these last points may be considered as very certain, especially since we had taken measures to keep the temperature very constant.

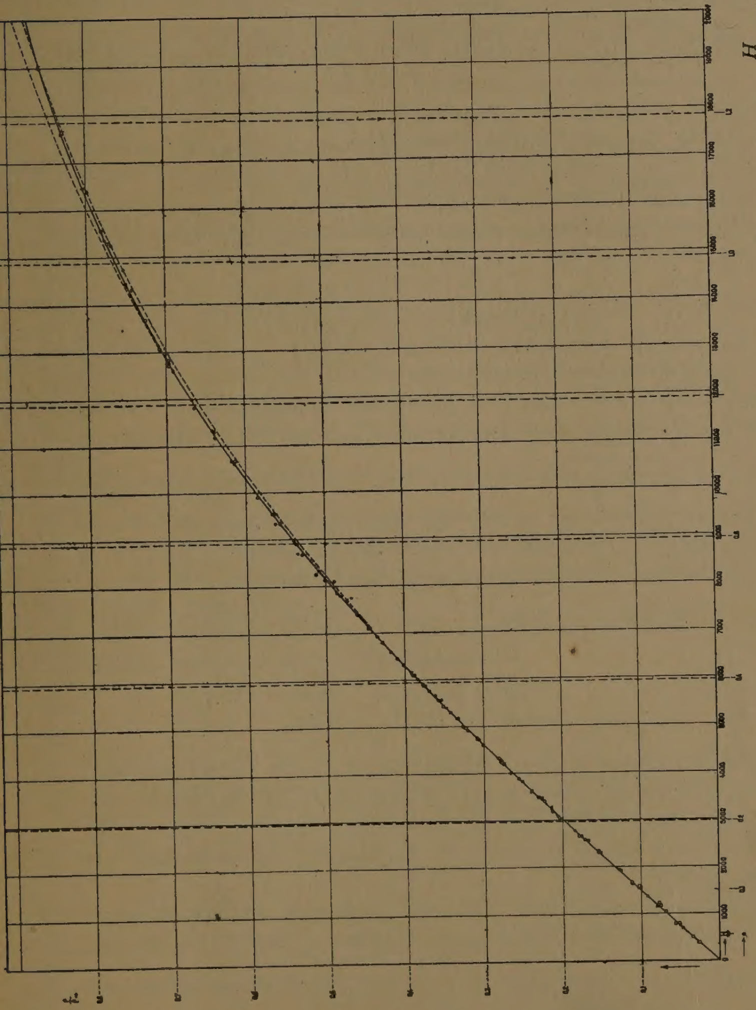

Fig. 1. Paramagnetic rotation of tysonite. All measurements have been combined in the curve. Abscissae $\frac{H}{T}$ and variable a. Ordinates: the rotations expressed in the saturation. The dotted curves are LANGEVIN curves with the same tangent at the origin as the tg hyp.

The points are observed values: □ for $T = 4°.21$, ○ for $T = 1°.71$, △ for $T = 1°.41$, ▽ for $T = 1°.39$.

The temperatures have been calculated under the assumption that the carrier of the magnetism is 1 BOHR magneton.

The two dotted curves are LANGEVIN curves, which have the same tangent at the origin as the hyperbolic tangent (the tangent in the origin seems to be well established).

The lowest curve passes through the last point; it is however not good, evidently being too low for the measurements taken as a whole, corresponding to the mean $\frac{H}{T}$ values. The highest curve represents very well the measurements up to $\frac{H}{T} = 10000$, but it is not good for higher values of $\frac{H}{T}$.

It is evident that no LANGEVIN curve gives such a strong curvature for the high values of $\frac{H}{T}$ as the experimental curve.

In the case of tysonite the paramagnetic rotation is very well represented by the law:

$$\varrho = (\varrho_\infty)_{\lambda,T}\, tgh\, a \quad ; \quad a = \frac{\Sigma_\infty H}{RT}$$

and Σ_∞ seems to be the BOHR magneton.

It is necessary to investigate the paramagnetic rotation of other crystals.

If the law found above is exactly valid for tysonite, which is very probable, then the saturation constant is determined by the ratio $\frac{\varrho}{tgh\, a}$ which is a constant for a given temperature and a given wavelength. The values obtained are given below expressed in radians. They refer to the thicket plate (e = 1.866 mm, at room temperature).

λ	$T_k = 77{,}55°$	$20{,}36°$	$4{,}21°$	$1{,}71°$	$1{,}41°$	$1{,}39°$
6249 Å			$-14{,}66\pi$			
5328,5 Å		$-24{,}61\pi$	$-21{,}81\pi$	$-19{,}61\pi$	$-18{,}74\pi$	$-18{,}73\pi$
4258,9 Å	$-51{,}60\pi$	$-45{,}21\pi$	$-40{,}02\pi$	$-36{,}01\pi$		

The numbers given for the temperatures of 77.55° (liquid nitrogen) and of 20.36° (liquid hydrogen) are the results of measurements made with different wavelengths in a field of 26.73 kilogauss. The rotations for 5328.5 Å and 4258.9 Å have been read on the full curve and then divided by tanh a.

For one and the same wavelength the saturation rotation decreases with the temperature and therefore the rotation ϱ also decreases with the temperature for a given value of $\frac{H}{T}$. For a given value of H however it increases up to the temperature 1.39°.

The decrease of ϱ_∞ with the temperature may be easily explained: the paramagnetic rotation is caused by the carriers of the magnetic moment, but the paramagnetic phenomenon manifests itself optically indirectly through the dispersion of the light. In order that a rotatory power can be observed, it is necessary, that one or more *active* absorption bands exist. By active is meant ,,which absorb to a different degree opposite circular polarised rays". The variability of ϱ_∞ is a manifestation of the fact, that the active absorption bands are not independent of the temperature, which moreover is evident for all bands in the visible spectrum. This change with the temperature might consist of a displacement in the spectrum, but this could not be great and could have only slight influence. The intensity of the bands in particular must vary and the decrease of ϱ_∞ is the proof of a decrease of the absorption. It is impossible to extrapolate and to say before hand whether the intensity of the bands approaches a finite limiting value or that it always decreases as the temperature approaches zero or that it passes perhaps through a minimum.

The variability of ϱ_∞ explains why the rotation in weak fields or at less low temperatures does not exactly follow the law of CURIE.

First we have plotted the curves for $\frac{1}{\varrho}$ as a function of T for a constant H, and it might be thought that the deviation from the rectilinear law, which is accentuated at very low temperatures, is caused by a cryomagnetic anomaly. The explanation however is quite otherwise : the deviation from the rectilinear law is caused 1st by the approach of saturation 2nd by the decrease of the absorption. In reality, as long as $\frac{H}{T}$ is not too large, the law of CURIE is obeyed for the magnetisation which is the primary cause of the optical effect (at the origin the tanh.curve coïncides with its tangent) but not of the magnetic rotatory power; the absorption makes the effect more complicated.

Finally we wish to express our thanks to Miss RIETVELD for her valuable assistance in the measurements.